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Anomalous course of the reaction between diethyl sodiothiophosphite and p-chlorobenzenesulfonyl chloride.

L. Al'mashi and A. Gants (Chem. Inst., Acad. Sci., Cluj). Invest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1585-3.

Cf. Ionescu et al. Studii si cercetari Chim. Cluj, 3, 159(1957), and 3, No.1, 135 (1957), Saunders et al. J. Chem. Soc. 1948, 629; Hoffmann et al. JACS 78, 6413 (1956).

All the reactions were run under H_2 for a suspension of 140 g. $(EtO)_2P(S)H$ in 250 ml. C_6H_6 was added an unstated amt. of $p-ClC_6H_4SO_2Cl$ and after 1 hr. of further heating the mixt. was filtered, the ppt. taken up in hot H_2O and acidified with HCl yielding 72 g. $p-ClC_6H_4SO_2H$, m. $96-8^\circ$. The org. layer gave 14 g. $(p-ClC_6H_4)_2SO_2$, m. 186° . Distn. of the mother liquor gave a range of fractions from which were isolated: $(EtO)_2P(S)Cl$, b_p $74-5^\circ$, n_D^{20} 1.4685 (with $p-ClC_6H_4SO_2H$ this gave $p-ClC_6H_4SO_2NH_2(2)(OEt)_2$, m. 95°), $(EtO)_3P$, b_p $88-9^\circ$, n_D^{25} 1.4481, d_{25}^{25} 1.0773, some unreacted $p-ClC_6H_4SO_2Cl$; $p-ClC_6H_4SO_2Et$, $b_{1.5}$ $112-4^\circ$, 1.5260 , 1.5269 , and an unidentified substance $C_{12}H_{12}O_4$, $b_{1.5}$ $123-8^\circ$, 1.5020 , 1.5004 . Thus the main reaction is the reduction of the sulfonyl chloride and chlorination of the thiophosphite salt. No reaction took place when $p-ClC_6H_4SO_2H$ and $(EtO)_2P(S)Cl$ were refluxed in C_6H_6 .

Passage of O_2 into 130 g. MeCN and 350 g. PCl_3 at 20° gave 2-4 g. high boiling residue. Combined products from many runs were distd. yielding some $POCl_3$ during each such distn. along with a product, b_{p-4} $68-75^\circ$, which with $EtOH$ gave $(EtO)_3PO$. The product formed in the reaction of MeCN could not be obtained in a pure state since on being heated it dissociated into $POCl_3$ and MeCN; however since it contained H, it is suggested that the substance may be $Et_3(COEt)(H)C(CH_3)_2POCl_2$. Similar reaction with EtCN gave 3.2% $C_3H_5Cl_3OPH$, b_3 $78-80^\circ$, d_{20} 1.4932, n_D^{20} 1.4918 evidently $EtCCl:HPOCl_2$, on the basis of its infrared spectrum. Reaction with PhCN gave a low yield of $PhCCl:HPOCl_2$, $b_{2.5}$ $140-5^\circ$, 1.4973, 1.5850. PrCN gave a low yield of $C_3H_7(CN)POCl_2$, $b_{1.5}$ $110-2^\circ$, 1.3998, 1.4903. BuCN gave 24.4% $C_4H_9(CN)POCl_2$, b_3 $135-55^\circ$, which on fractionation gave a range of fractions of approximately the same compn.

organophosphorus
 Allyl esters of some alkyl-, alkenyl- and chloroalkylphosphonic acids.

L. Z. Scherovskii and Yu. M. Minev'ev. Zhur. Obshchei Khim. 29, 2152-4(1959).
 of. Toy et al. JACS 76, 2191(1954); Castro et al. ibid. 72, 2275(1950);
 USPat 2,601,520 (CA 46, 8417(1952), and 2,699,714(CA 48, 12166(1954))).
 The reaction of PCl_3 and O_2 with appropriate alkanes gave RPOCl_2 (mixts.
 of isomers) which were used in the following syntheses. Addn. of 16.1 g.
 $\text{C}_7\text{H}_{15}\text{POCl}_2$ to 19.3 g. $\text{CH}_2=\text{CHCH}_2\text{OH}$ and 26.3 g. pyridine at $0-5^\circ$ gave after
 1 hr. stirring, followed by addn. of 10 ml. H_2O , sepn. of the org. layer
 and washing this with 3% NaOH in 10% NaCl, 14.1 g. $\text{C}_7\text{H}_{15}\text{PO}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$,
 b_3 117-23°, d_{20} 0.9986. Similarly 33.5 g. $\text{C}_6\text{H}_{11}\text{POCl}_2$ gave 8.9 g. $\text{C}_6\text{H}_{11}\text{PO}-$
 $(\text{OCH}_2\text{CH}=\text{CH}_2)_2$, b_4 130°, 1.0549. $\text{C}_3\text{H}_7\text{ClPOCl}_2$ (prepd. as above from propylene
 propylene) similarly gave in the presence of Et_3N 60% $\text{C}_3\text{H}_7\text{ClPO}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$,
 b_3 113-5°, d_{20} 1.122, n_D^{20} 1.4598. $\text{C}_4\text{H}_9\text{ClPOCl}_2$ (from 1-butene) similarly
 gave 18.6% $\text{C}_4\text{H}_9\text{ClPO}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$, b_3 117-8°, 1.0980, 1.4618. Passage of
 $\text{C}_3\text{H}_7\text{ClPOCl}_2$ over activated C at 250-300° and 50 mm. gave 50.7% $\text{H}_2\text{CCH}=\text{CHPOCl}_2$,
 b_{16} 75-7°, 1.3343, 1.4815, which with $\text{CH}_2=\text{CHCH}_2\text{OH}$ at -15° (excess ROH) gave
 54.6% $\text{H}_2\text{CCH}=\text{CHPO}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$, $b_{3.5}$ 98°, 1.0375, 1.4558. (cf. Kamai et al,
 Doklady Akad. Nauk SSSR 89, 309 (1953) gives for $\text{CH}_2=\text{CHCH}_2\text{PO}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$,
 b_3 94-5°, 1.0050, 1.4600.).

Jan
 Synthesis of organophosphorus compounds from hydrocarbons and their derivatives. XII. Oxidative chlorophosphonation of halogenated alkanes. Yu. M. Zinov'ev and L. Z. Seberovskii. Zhur. Obshchei Khim. 29, 2643-6 (1959). cf. 29, 2088 (1959).

Passage of O_2 at $0-5^\circ$ into 63.8 g. BuBr and 400 g. PCl_3 until the reaction stopped, gave 42.3 g. crude product, b_4 $110-45^\circ$, comprised of isomers of $C_4H_9BrPOCl_2$, b_4 $109-132^\circ$ (5 fractions are listed in this range), d_{20}^{20} 1.6322-1.6607, n_D^{20} 1.5103-1.5197. Passage of O_2 at -20° into 32 g. Me_3CH and 200 g. PCl_3 gave 6.7 g. $C_3H_7FPOCl_2$, b_{19} $80-3^\circ$, 1.3091, 1-fluoro-2-chloroethane similarly gave 11.7% $C_2H_5FCIPCl_2$, b_{30} $98-100^\circ$, 1.6279, 1.4600. $MeEtCHCl$ gave 35.4% $C_4H_9ClPOCl_2$, $b_{2.5}$ $85-93^\circ$, 1.3903, 1.4905, identical with $MeCHCl_2$ gave 2% $CHCl_2CH_2POCl_2$, b_2 $78-80^\circ$, 1.6877, 1.4813, which with EtOH gave $CHCl_2CH_2PO(OEt)_2$, 31%, b_4 $95-7^\circ$, 1.2398, 1.4360. $MeCCl_3$ gave a low yield of $CCl_3CH_2POCl_2$, b_5 95° , 1.7398, -, which with EtOH gave $CCl_3CH_2PO(OEt)_2$, b_3 50° , n_D^{20} 1.4470. BuI not only failed to react with O_2-PCl_3 but inhibited the oxidation of PCl_3 .

Addition of dialkyl hydrogen phosphites to alkyl isothiocyanates.

K. A. Petrov and A. A. Meinyasheva. Zhur. Obshchei Khim. 29, 1819-21(1959).
 F&M Chadwick
 of. Shumskii et al. JACS 78, 1861(1956), and Shumskii et al. JACS 77, 3815(1955).

To an equimolar mixt. of $(RO)_2P(O)H$ and $R'NCS$ there was added dropwise $EtONa-EtOH$ until the exothermic effect terminated; after 2 hrs. at $105-10^{\circ}$, the cooled mixt. was washed with H_2O and extd. with Et_2O .

Evapn. and drying of the org. layer gave the following adducts:

54.4% $MeNHOSP(O)(OEt)_2$, $b_{0.2}$ $135-4^{\circ}$, d_{20} 1.1820, n_D^{20} 1.4998; $MeNHOS-P(O)(OCHMe_2)_2$, 46.3%, $b_{0.08}$ $113-5.5^{\circ}$, 1.1167, 1.4947; $MeNHOSP(O)(OBu)_2$, 57.7%, $b_{0.05}$ 140.5° , 1.0658, 1.4940; $CH_2=CHCH_2NHOSP(O)(OEt)_2$, 47.8%, $b_{0.07}$ $125-6^{\circ}$, 1.1422, 1.5120; $CH_2=CHCH_2NHOSP(O)(OCHMe_2)_2$, 46.4%, $b_{0.05}$ $125-4^{\circ}$, 1.0980, 1.5000. Heated with aq. HCl these hydrolyze to H_3PO_4 (isolated as trianiline salt, m. $175-6^{\circ}$). Treating 11.7 g. $MeNHOSP(O)(OEt)_2$ with 11.6 g. PCl_3 , the reaction being run in dry $COCl_2$, 2 hrs. at 65° , treatment with SO_2 to decompose any residual PCl_3 , and distn. in good vacuum, gave 59.5% $(EtO)_2POCl$, $b_{0.4}$ $50-60^{\circ}$ (crude), indicating the cleavage of the P-C bond.

Mixed anhydrides of carboxylic acids and acid esters of phosphoric and methylphosphonic acids. A new method of preparation of pyrophosphates. K. A. Petrov and A. A. Meinyshova. Zhur. Obshchei Khim. 29, 1822-3(1959). In view of conflicting descriptions of various acylphosphates in the literature (cf. Kabachnik et al. this j. 26, 120(1956); 26, 2228(1956); Zemlyanskii et al. this j. 26, 1677(1956); Schrader, Angew.Chem. 63, 471 (1950)), the prepn. of these substances was developed as follows. To 0.11 mole RCO_2Ag in 50 ml. abs. Et_2O there was added dropwise 0.1 mole desired chlorophosphate or phosphonic chloride at $35-40^\circ$, the mixt. being stirred until a test sample fails to show free Cl ions (6 hrs. to several days). After filtration, the soln. was kept in vacuo for several hrs. yielding the following acylated products which were analyzed directly without distn.: $(\text{MeO})_2\text{P}(\text{O})\text{OAc}$, d_4^{20} 1.2990, n_D^{20} 1.4070; $(\text{EtO})_2\text{P}(\text{O})\text{OAc}$, d_4^{14} 1.1678, n_D^{17} 1.4117; $\text{PrOPMe}(\text{O})(\text{OAc})$, d_4^{20} 1.5120, n_D^{20} 1.4566; $\text{MeOPMe}(\text{O})(\text{OAc})$, d_4^{14} 1.2618, n_D^{14} 1.4212; $(\text{EtO})_2\text{P}(\text{O})\text{O}i\text{C}_3\text{H}_7$, $d_4^{17.5}$ 1.3074, n_D^{19} 1.3750; $(\text{EtO})_2\text{P}(\text{O})\text{OMe}$, d_4^{16} 1.1900, n_D^{16} 1.4910. The products decompose on attempted distn. and form $(\text{RCO})_2\text{O}$ and a sym. pyrophosphate. Heating 17 g. $(\text{Me}_2\text{N})_2\text{POCl}$ with 20 g. dry AgOAc in dry C_6H_6 at reflux gave after filtration 74.6% Me_2NAs . Heating 0.1 mole $(\text{RO})_2\text{POCl}$ or similar chloride with 0.18 mole dry AgOAc in C_6H_6 6-8 hrs., filtration and distn. gave As_2O and $(\text{RO})_2\text{P}(\text{O})\text{OP}(\text{O})(\text{OR})_2$. $\text{Pb}(\text{OAc})_2$ may be used similarly instead of the Ag salt; Ag_2CO_3 and PbO_2 also gave similar results; the Pb salts generally require 12-20 hrs. for the reaction. The following were reported: $[(\text{EtO})_2\text{P}]_2\text{O}$, 90%, b_p 144-5°, d_4^{20} 1.2110, n_D^{19} 1.4223; tetra-*iso*-Pr analog, 54%, $b_{2.5}$ 140-1°, $d_4^{20.5}$ 1.6250, $n_D^{20.5}$ 1.4200; $[(\text{MeO})\text{PMe}(\text{O})]_2\text{O}$, b_4 157.5-5°, d_4^{17} 1.3172, n_D^{17} 1.4370; $[(\text{EtO})(\text{Et}_2\text{N})\text{P}]_2\text{O}$, 39%, b_2 153-3.5°, d_4^{18} 1.2102, n_D^{18} 1.4402; $[(\text{PrO})\text{PMe}(\text{O})]_2\text{O}$, 75%, b_2 143-4°, d_4^{18} 1.2212, n_D^{18} 1.4340. The pyro derivs. are thermally unstable; the tetra-*iso*-Pr ester decamps. at 190°; the di-Nt bis-diethylamide) member decamps. at 230°; di-Me Me pyrophosphate at any vacuum distn., yielding some $\text{MePO}(\text{OMe})_2$.

*synthesis***Esters of alkylcyanophosphonic acids.**

K. A. Petrov, L. G. Gatsenko and A. A. Reimysheva. Zhur. Obshchei Khim. 29, 1827-31 (1959). cf. this j. 26, 3377 (1954).

The Arbuzov reaction was extended to cyano deriva. of trivalent P.

To 21.5 g. $(\text{EtO})_2\text{PCl}$ in dry Et_2O was added 23.6 g. dry AgCN and the whole refluxed 12 hrs. The filtrate gave 47.5% $(\text{EtO})_2\text{PCN}$, b_p 51-5°, d_{20}^{20} 1.0220, n_D^{20} 1.3875, which is rapidly attacked by H_2O . Similarly were obtained: $(\text{iso-PrO})_2\text{PCN}$, 44%, b_p 62-4°; $(\text{PrO})_2\text{PCN}$, b_p 80-2°, $d_{24.5}^{24.5}$ 0.9835, $n_D^{21.5}$ 1.4270; PrOP(CN)_2 , 70%, b_p 61°, d_{20}^{20} 1.0335, n_D^{20} 1.4504.

The latter decomposes on storage and is vigorously attacked by H_2O ; it forms a complex with cuprous halides. Similarly was prepd. EtOP(CN)_2 , b_p 51.5-2°, d_{20}^{20} 1.1349, n_D^{20} 1.4535. Heating 17.5 g. $(\text{PrO})_2\text{PCN}$ and 70 g. NaI in sealed tube 10 hrs. at 140° gave 80% $(\text{PrO})_2\text{P(O)CN}$, b_p 95°, $d_{24.5}^{24.5}$ 1.0385, $n_D^{24.5}$ 1.4125; reaction run at 150° also gave some NaP(O)(O)OPr but the yield was very low. The product is rapidly hydrolyzed by H_2O ; it reduced KMnO_4 ; it is decomposed by Cu_2Cl_2 .

The ester in SOCl_2 was treated with Cl_2 at 20° and finally at 60°, yielding on distn. PrCl , POCl_3 and NaPOCl_2 (b_p 162°, n_p 51-2°).

The latter on hydrolysis gave NaPO_3H_2 , m_p 102-5°. Similarly $(\text{EtO})_2\text{PCN}$ and NaI in 8 hrs. at 140° gave NaP(O)(O)OEt , b_p 73-4°, d_{20}^{20} 1.1884, n_D^{19} 1.4206. EtI gave in 10 hrs. at 140° EtP(O)(O)OEt , b_p 79-60°, d_{20}^{20} 1.0795, n_D^{20} 1.4196. $(\text{PrO})_2\text{PCN}$ and PrI in 12 hrs. at 170° gave PrP(O)(O)OPr , b_p 99-102°, d_{20}^{20} 1.0135, n_D^{20} 1.4300 (hydrolysis gave PrPO_3H_2 , m_p 66°; ammonium salt, m_p 223-5° (from PrCN)). The above alkylcyano deriva. are properly describable as phosphinates, owing to the attachment of 2 C-contg. groups to the P atom.

original

Anhydrides of phosphonoisobutyric acid. III.

K. A. Petrov, A. A. Neimysheva and E. V. Smirnov. Zhur. Obshchei Khim. 29, 1491-4 (1959). or. 29, 301 (1959).

To 23.4 g. $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CHMeCO}_2\text{Me}$ in 25 ml. OCl_4 there added over 0.5 hr. with H_2O cooling 23.2 g. PCl_5 , after which the mixt. was heated on a water bath to 70° over 2 hrs. at kept at 70° 1 hr.; unreacted PCl_5 was decomposed with SO_2 and the mixt. was distd. yielding 74.5% $\text{MeOP}(\text{O})\text{Cl}-\text{CH}_2\text{CHMeCO}_2\text{Me}$, b_1 $104-5^\circ$, d_{25} 1.2675, n_D^{25} 1.4560, which may be stored without decomp. for long periods. Similarly, 17.8 g. $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CHMeCO}_2\text{Me}$ and 17.6 g. PCl_5 in 20 ml. OCl_4 in 3 hrs. on a steam bath gave 2 products; the 1st, b_0 $123-4^\circ$ (5.5 g.) contained more Cl than required for the above monochloride and even repeated fractionation failed to give the expected monochloride from it; the 2nd fraction, b_0 $165-4^\circ$ (4.7 g.) gave on redistn. some cyclic anhydride ~~MeOP(O)CH₂CHMeCO₂Me~~ $\text{MeOP}(\text{O})\text{CH}_2\text{CHMeCO}_2$, $b_{0.1}$ $100-2^\circ$, d_{22} 1.5004, n_D^{25} 1.4520, which with H_2O yields the free acid which was shown to be dibasic by titration. If the hydrolyzate is treated with AgNO_3 there is formed the di-Ag salt, $\text{C}_5\text{H}_9\text{O}_5\text{P}(\text{O})\text{Ag}_2$, which with NaI in CHCl_3 gave the original $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CHMeCO}_2\text{Me}$. Reaction of 21.5 g. $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CHMeCO}_2\text{Et}$ and 17.6 g. PCl_5 in 20 ml. OCl_4 under the conditions of the 1st expt. above gave 78.5% $(\text{EtO})\text{P}(\text{O})\text{ClCH}_2\text{CHMeCO}_2\text{Et}$, b_1 $115-6^\circ$, d_{22} 1.1895, n_D^{25} 1.4489. This heated at $150-70^\circ$ gave EtCl and the cyclic anhydride $(\text{EtO})\text{P}(\text{O})\text{CH}_2\text{CHMeCO}_2$, a liquid which is hydrolyzed by H_2O yielding $(\text{EtO})(\text{HO})\text{P}(\text{O})\text{CH}_2\text{CHMeCO}_2\text{H}$, which titrates as a dibasic acid. Similar reaction of PCl_5 with $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CHMeCHMeCO}_2\text{Et}$ gave the ~~same~~ chloride, $(\text{EtO})\text{P}(\text{O})\text{ClCH}_2\text{CHMeCHMeCO}_2\text{Et}$, b_2 $150-2^\circ$, d_{19} 1.1617, n_D^{20} 1.4452, which heated to $160-90^\circ$ 6 hrs. gave EtCl and the anhydride $(\text{EtO})\text{P}(\text{O})\text{CH}_2\text{CHMeCHMeCO}_2$, $b_{2.5}$ $129-30^\circ$, d_{20} 1.2304, n_D^{19} 1.4323.

Reaction of phosgene with trialkyl phosphites.

K. A. Petrov, N. K. Bliznyuk and V. E. Burygin. Zhur. Obshchei Khim. 29, 1486-91 (1959). Cf. Kabachnik et al. Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1957, 48.

The reaction described by Kabachnik (cf. ref. above) is erroneous and the reaction of COCl_2 with $(\text{RO})_3\text{P}$ yields not acylphosphonates but CO , ROCl and $(\text{RO})_2\text{POCl}$. Passage of 14.65 g. dry COCl_2 into 18.6 g. $(\text{MeO})_3\text{P}$ over 3 hrs. with H_2O cooling gave 97% MeOCl and 96% CO as well as 76% $(\text{MeO})_2\text{POCl}$, $b_{12} 70^\circ$, $d_{20} 1.5320$, $n_D^{20} 1.4125$. The latter also formed from SO_2Cl_2 and $(\text{MeO})_3\text{P}$. This chloride and PhNH_2 in Et_2O gave 79.5% $(\text{MeO})_2\text{PONEPh}$, $m. 88.5^\circ$ (from H_2O). Addn. dropwise of 18.4 g. $(\text{MeO})_3\text{P}$ to 14.45 g. $(\text{MeO})_2\text{POCl}$ heated on a steam bath resulted in a reaction which began at 90° and was complete in 30-40 min. yielding 80% MeOCl , 5.5 g. $\text{MePO}(\text{OMe})_2$, $b_{12} 68-7^\circ$, $d_{20} 1.1785$, $n_D^{20} 1.4191$ (free acid forms an aniline salt, $m. 148-50^\circ$), and some 9 g. evidently $[(\text{MeO})_2\text{PO}]_2$, $b_{0.6} 114-5^\circ$, $d_{20} 1.5360$, $n_D^{20} 1.4254$; the latter on repeated distn. gave more $\text{MePO}(\text{OMe})_2$ (some 40%) and 50% unchanged bisphosphonate ester. Some insol. residual solid was found in the distn. flask, possibly $(\text{MeOPo})_2$. Treatment of 2.18 g. $[(\text{MeO})_2\text{PO}]_2$ in CCl_4 with 1.85 g. SO_2Cl_2 with ice cooling gave 17% $(\text{MeO})_2\text{POCl}$. The $\text{P}=\text{O}$ bisphosphonate is cleaved by H_2O evidently to $(\text{RO})_2\text{P}=\text{O}$ and $(\text{RO})_2\text{PO}_2\text{H}$ since the products reduce Hg^{++} . The bisphosphonate is cleaved by Cl_2 to $(\text{MeO})_2\text{POCl}$. Reaction of 9.9 g. COCl_2 with 16.6 g. $(\text{EtO})_3\text{P}$ gave 94% EtOCl , 90% CO and 76% $(\text{EtO})_2\text{POCl}$ (amide, $m. 94-5^\circ$). Reaction of 17.25 g. $(\text{EtO})_2\text{POCl}$ with 16.6 g. $(\text{EtO})_3\text{P}$ at 155° gave 24% EtOCl , 3.9 g. $\text{EtPO}(\text{OEt})_2$ (free acid forms an aniline salt, $m. 143-5^\circ$), 16 g. $[(\text{EtO})_2\text{PO}]_2$, $b_{0.6} 139^\circ$, $d_{20} 1.1492$, $n_D^{20} 1.4200$; the latter behaves like the Me analog and with SO_2Cl_2 readily yields $(\text{EtO})_2\text{POCl}$ (29%).

0.5 sample

Syntheses based on the ethyl ester of hydroxymethylphosphonic acid.

N. A. Arbusov and N. P. Bogenestseva (State Univ., Kazan). Zhur. Obshch. Khim. 29, 2617-22 (1959). cf. Abramov, this j. 22, 647 (1952) and Uchen. Zapiski Kazan. Gos. Univ., 108, No.1, Khimiya, No.4, 77 (1948).

To 2.3 g. Na in 50 ml. dry Et₂O was added 14 g. (EtO)₂PHO and after the disappearance of Na the cooled soln. was treated with 3 g. polyoxymethylene which led to a vigorous reaction yielding a clear soln. of Na salt of HOCH₂P(O)(OEt)₂ (I), which was used directly below. Treatment of I with 19 g. (EtO)₂POCl gave after sepn. of NaCl 23% (EtO)₂P(O)CH₂OP(O)(OEt)₂, b_{1.5} 162.5-3.5°, d₂₀²⁰ 1.1776, n_D²⁰ 1.4283; the product decomposes during each redistn. yielding a fraction, b₂₋₃ 74-6°, which does not appear to be any known substance; it was not identified further. I from 28 g. (EtO)₂PHO was treated with 24.5 g. ClCH₂CO₂Et, yielding after 1 hr. on a steam bath 43% (EtO)₂P(O)CH₂OCN₂CO₂Et, b_{1.5} 147-9°, 1.1496, 1.4348. I and ClCO₂Et gave some (EtO)₂CO and 17.24% (EtO)₂P(O)CH₂OCO₂Et, b_{11.5} 152-3°, 1.1246, 1.4215, which decomposes on redistn. yielding a constant fraction, b₄ 68°, 0.9032, 1.4150 and one b₂ 129-30°, 0.8629, 1.4265, which appears to be close to EtOCH₂P(O)(OEt)₂. I and ClCH₂CH₂OH gave a substance close in compn. to HOCH₂P(O)(OEt)₂, b₄ 141-1.5°, 1.1700, 1.4370, which decomposes during redistn. I (4 moles) and 1 mole SiCl₄ gave an undistillable oil which solidified to a friable solid; a low yield of liq. product was isolated which b₄ 140.5-1°, 1.1527, 1.4325, and was apparently HOCH₂P(O)(OEt)₂. I (3 moles) and 1 mole PCl₃ gave mainly HOCH₂P(O)(OEt)₂, b₃ 136-8°, 1.1380, 1.4283, and evidently some (EtO)₂PHO. Passage of COCl₂ into I at room temp. gave C₆H₁₅O₅P, b_{1.5} 133-6°, 1.1603, 1.4270, which was possibly (EtO)₂P(O)CH₂OCO₂CH₂P(O)(OEt)₂ or (EtO)₂P(O)CH₂OCN₂P(O)(OEt)₂. I (from 24 g. ester) and 10 g. SOCl₂ gave Et₂SO₃, Et₃PO₄, HOCH₂P(O)(OEt)₂ and 2 new products: a liquid, b_{2.5} 173°, 1.1947, 1.4360 (II), and a solid (III), m. 150-1°. II kept in ampul 6 months gave III. II is possibly (EtO)P(O)(CH₂OH)OCN₂P(O)(OEt)₂, while III may be cyclic [(EtO)P(O)CH₂]₂.

2

addn. of 65 g. $(EtO)_3P$ to 42.5 g. $AcOCH_2Cl$ and heating 4 hrs. on a steam bath gave a range of fractions from which were isolated $(EtO)_3P$ and 12 g. of rather unstable $AcOCH_2P(O)(OEt)_2$, b_3 180-3°, n_D^{20} 1.4375, d_{20}^{20} 1.1420, which on repeated distn. yields a $C_5H_{11}O_3P$, b_3 193-9°, 1.4426, 1.1705. I (from 21 g. ester) and 9.16 g. $AcOH$ gave a ppt. of $NaOAc$ which was sepd. The filtrate was refluxed 3 hrs. on a steam bath with 5 drops $EtONa$ soln., yielding a low yield of III, m. 145-50°, obtained from crystn. of a fraction, $b_{7.5}$ 138-43°. Refluxing $HOCH_2P(O)(OEt)_2$ with H_3PO_4 failed to yield any III. I (from 42 g. ester) was treated with 24 g. $AcCl$; after 2 hrs. the pptd. $NaCl$ was sepd. and the filtrate treated with a little H_3PO_4 and heated on a steam bath 4 hrs. yielding 14.4 g. $EtOAc$ and a fraction, b_5 105-6°, which left an undistillable residue; this allowed to stand 5 months became distillable and yielded a fraction b_4 125-35°, which on standing pptd. III, m. 145-50°. Refluxing $AcOCH_2P(O)(OEt)_2$ (3 g.) with 2 ml. $EtONa-EtOH$ soln. 5 hrs. on a steam bath gave an undistillable mass which gave some 0.3 g. III. The same formed from this acetate and H_3PO_4 .

organophosphorus

Thermographic study of isomerization reaction of esters of glycol hydrogen phosphite, containing a six-membered ring, under the action of alkyl halides.

B. A. Arbuzov, V. M. Zorcastrova and M. K. Saikina (V.I. Ul'yanov-Lenin State Univ., Kazan). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1959, 1579-84. cf. 1957, 1042.

A thermographic study was made of the reaction of HX with $\text{CH}_2(\text{CH}_2\text{O})_2\text{P}(\text{OR})_2$ (I) and $\text{CHMeCH}_2\text{CH}_2\text{OP}(\text{OR})_2$ (II). II (R-Me, Et, Pr) and I (R-Me and PhCH_2) produce only a single thermographic peak in their reactions and gave the previously reported esters of alkylphosphonic acids with a 6-membered ester ring, indicating that the Arbuzov reaction occurs in these cases without ring opening. Curiously, I (R-Ph) reacted with NaI (and EtBr) with a single thermographic peak and gave the product of ring opening $\text{ICH}_2\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OPh})\text{Me}$, b_2 152-3°, n_D^{20} 1.5510, d_4^{20} 1.6155. Further heating of this product led to decompn. Reaction of EtBr with $\text{o-C}_6\text{H}_4\text{O}_2\text{P}(\text{OR})_2$ also gave a single thermographic peak and yielded $\text{o-C}_6\text{H}_4\text{O}_2\text{P}(\text{O})\text{Et}$, b_{15} 154-7°, 1.5200. The thermograms are reproduced. The following esters are reported: II, R-Me, b_{15} 62°, d_4^{20} 1.1092, n_D^{20} 1.4420; R-Et, b_2 63-4°, 1.0696, 1.4410; R-Pr, $b_{6.5-7}$ 72-2.5°, 1.0425, 1.4455; I, R-Me, b_{11} 50-1°, 1.1758, 1.4465; R-Ph, $b_{1.5-2}$ 105-8°, n. 45-8°; R- PhCH_2 , b_{13-14} 147-8°, 1.1678, 1.5290; $\text{o-C}_6\text{H}_4\text{O}_2\text{P}(\text{OR})_2$, b_{11} 86°, d_4^{20} 1.2420, n_D^{17} 1.5065; $\text{CHMeCH}_2\text{CH}_2\text{OP}(\text{O})\text{MeO}$, b_5 109-11°, n. 40-1°; $\text{CHMeCH}_2\text{CH}_2\text{OP}(\text{O})\text{EtO}$, b_1 103-5°, n_D^{20} 1.4500, d_4^{20} 1.1541; $\text{CHMeCH}_2\text{CH}_2\text{OP}(\text{O})\text{PrO}$, b_1 106-7°, 1.4505, 1.0995; $\text{CH}_2(\text{CH}_2\text{O})_2\text{P}(\text{O})\text{Me}$, n. 97-9.5°; $\text{CH}_2(\text{CH}_2\text{O})_2\text{P}(\text{O})\text{CH}_2\text{Ph}$, n. 137.5° (formed from either PrCH_2Br or PhCH_2Cl).

Janopur
Reaction of esters of phosphorous acid with alkyl halides studied by the method of thermography. I. Reactions with aromatic phosphites.

B. A. Arbuzov and A. V. Fushenkova (State Univ., Kazan). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1928-34.

Thermograms are reported for the reaction of RX with $(RO)_3P$ contg. aryloxy groups. The thermograms show 2 exothermic effects, the 1st of these at the initial formation of the adduct, the 2nd at this decompn. The peaks recorded in this manner indicate that the adducts decrease in their thermal stability in the sequence: $(PhO)_3P$, $(PhO)_2POEt$, $PhOP(OEt)_2$. The effective reaction temp. rises with increase of the size of alkyl radical in RX. Its variation with change of X is conventional. Esters used were: $(PhO)_3P$, $(o-MeC_6H_4O)_3P$, $(PhO)_2POEt$ and $PhOP(OEt)_2$.

II. Reactions with aliphatic phosphites. Ibid. 1958-61.

Thermograms are shown for reactions of RX with $(MeO)_3P$, $(EtO)_3P$, as the ester components. The halide components were: MeI, EtI, iso-PrI, BuI, iso-BuI, EtBr, PrBr, $PhCH_2I$, $PhCH_2Br$, $PhCH_2Cl$, Ph_3CCl , Ph_2CCl , $CH_2=CHCH_2I$, MeBr, EtCl, $BrCH_2CHBrOEt$, $ClCH_2CHClOEt$, $BrCH_2CHBrCH_3$, ICH_2CO_2Et , $MeCH_2CO_2Et$, and $p-MeO_2C_6H_4SO_2Et$. The thermograms show 2 exothermic effects (cf. preced. abstr.), which with rapid heating can fuse into a single peak. A similar 2-peak thermogram is obtained from $EtP(OEt)_2$ and Et_2POEt in reaction with EtI; the 1st peak corresponds to formation of very hygroscopic solid adduct. Reactions of $(RO)_3P$ with R'_2CHX show 3 exothermic effects of which only the 1st is that caused by the Arbuzov reaction proper, i.e. formation of the phosphonate. The other 2 effects may be caused by stepwise cleavage of the di-Et ester to mono-Et ester and finally to the free acid under influence of heat. This is confirmed by a single thermal effect in the reaction of $(MeO)_3P$ which yields the di-Me ester which cannot form C_2H_4 as a pyrolysis product. The reaction with $p-MeO_2C_6H_4SO_2Et$ gave but 1 thermal effect with $(EtO)_3P$ at 152° ; the mixt. exploded at 300° . If the reaction is run very slowly, 2 effects appear: 155° and 194° .

Organophosphorus derivatives of ethylamine. Diethylamides of α -phosphorus.

N. P. Gorchukin and G. S. Bobchenko (Chem. Inst., Acad. Sci., Kazan). Doklady Akad. Nauk S.S.S.R. 129, 569-71 (1959).

Heating 10 g. $\text{EtOP(O)(NEt}_2)_2$ with 25 g. Et_2NH in sealed tube 16 hrs. at 90° gave 67.5% $\text{C}_{14}\text{H}_{25}\text{N}_4\text{O}_2$, $b_{1.3}$ 165° , n_D^{20} 1.4635, d_{20} 0.9895. Similarly $\text{EtOP(O)(NEt}_2)_2$ gave 73% $\text{C}_{14}\text{H}_{25}\text{N}_4\text{O}_2$, b_1 176° , 1.4695, 0.9761. These products are described as adducts to the above imides, presumably at the oxiridine rings. The following products were prep. conventionally (cf. Section, Ann. 566, 210(1950), and Gorchukin, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1956, 538; also K. A. Kornev and L. D. Protchenko, Ukrain. Khim. Zhur. 22, 782 (1956); $\text{EtOP(NEt}_2)_2$, $b_{1.1}$ $76-7^\circ$, 1.4810, 1.0444, 70%; $\text{EtOP(O)(NEt}_2)_2$, b_2 $91-2.5^\circ$, 1.4712, 1.1688, 70%; $\text{EtOP(NEt}_2)_2$, b_1 $103.5-4.5^\circ$, 1.4681, 1.1362; $\text{EtOP(O)(NEt}_2)_2$, $b_{0.5}$ $105-6^\circ$, 1.4676, 1.1608, 80%; $\text{EtOP(S)(NEt}_2)_2$, $b_{0.2}$ $90-1^\circ$, 1.5198, 1.1662, 80%; $\text{EtOP(S)(NEt}_2)_2$, $b_{0.4}$ $103.5-4.5^\circ$, 1.5129, 1.1300, 80%; $\text{iso-EtOP(S)(NEt}_2)_2$, $b_{0.1}$ $79-80^\circ$, 1.5098, 1.1237, 60%; $\text{EtOP(S)(NEt}_2)_2$, $b_{0.2}$ $113.5-4.5^\circ$, 1.5087, 1.1646, 74%; $\text{EtOP(S)(NEt}_2)_2$, $b_{0.5}$ 89° , 1.5402, 1.1367. The structures of the adducts described in the 1st part are presumed to be $\text{ROP(O)(NNEt}_2\text{CH}_2\text{NEt}_2)_2$.

rearrangement
Rearrangement of esters of α -hydroxyalkylphosphonic acids into isomeric phosphates.

V. A. Kukhtin, V. S. Abramov and K. M. Spukhova (S.M. Zhov Chem. Tech. Inst., Karam), Doklady Akad. Nauk SSSR, 128, 1198-1200 (1959).

Heating $(HO)_2PNO$ with diacetyl in sealed tubes at 100° gave: $(MeO)_2P(O)OMe(OH)COMe$, b_p 116°, n_D^{20} 1.4330, d_{15} 1.2391; $(MeO)_2P(O)OMe(OH)COMe$, b_{10} 118-40°, 1.4445, 1.1397; and $(MeO)_2P(O)OMe(OH)COMe$, b_p 143°, 1.4480, 1.0641.

If the reaction is run at above 100° , the following products are formed:

$(MeO)_2P(O)OCMeMe$, b_{15} 132-3°, 1.4340, 1.2210; $(EtO)_2P(O)OCMeMe$, b_{10} 133-4°, 1.4330, 1.1148; and $(MeO)_2P(O)OCMeMe$, b_{10} 160-1°, 1.4370, 1.0172.

The formation of the 2nd group of products depends solely on the temp. ($125-130^\circ$), as at $90-100^\circ$ the products of the 1st type are formed regardless of the mode of reaction (refluxing in presence of $EtONa-EtOH$, heating in sealed tube, heating under a reflux condenser with or without added acetic C_6H_6 , in air or under H_2). The products of the 1st type contain an active HO group, shows intense absorption at 3390 cm^{-1} . The products of the 2nd type do not absorb in $3250-3300\text{ cm}^{-1}$ region, lack the HO group and on being hydrolyzed with $Na(OH)_2$ yield $(HO)_2P_2H$ as the Na salt. The products of the 1st type are isomerized into those of the 2nd type on being heated briefly with $EtOH-EtONa$, evidently through ionization of the alcoholic HO group, followed by the electronic shift through a nucleophilic attack by the negatively charged O atom on the positively charged neighboring P atom. The loss of the halide ion indicated by Bengelsohn (J. Org. Chem. 21, 473 (1956)) is not a necessary event for such reactions, and the mere presence of electron attracting groups, like the carbonyl, is sufficient.

The yields were 50-80%.

Yakovlev
**Reaction of dialkyl hydrogen phosphites with aldehydes and ketones. XX.
 Esters of some α -hydroxyalkylthiophosphonic acids.**

V. S. Abramov and V. K. Khairullin (Chem. Tech. Inst., Kazan). Zhur. Obshch. Khim. 29, 1599-604 (1959). cf. 28, 1059 (1958).

Passage of dry H_2S into $(RO)_2PCl$ in Et_2O until all traces of HCl disappear from the effluent gas, results in $(RO)_2PHS$ formation; if the reaction is run in the presence of pyridine to take up the HCl formed, the product is contaminated with some $[(RO)_2P]_2S$. The resulting $(RO)_2PHS$ were undistillable sirups. Thus were prepd.: $[Me_2C(CCl_3)O]_2PHS$, $[(CH_2)_4C(CCl_3)O]_2PHS$, m. $50-5^\circ$, and $(PhO)_2PHS$. These were kept several days in sealed ampuls with aldehydes or ketones, yielding the following adducts: $(PhO)_2P(S)CH(OH)CCl_3$, m. $124-6^\circ$; $[Me_2C(CCl_3)O]_2P(S)CH(OH)CCl_3$, m. $151-3^\circ$; $[Me_2C(CCl_3)O]_2P(S)-CHPhOH$, m. $167-5^\circ$; $[Me_2C(CCl_3)O]_2P(S)CHMe_2OH$, m. $153-5^\circ$; $[Me_2C(CCl_3)O]_2P(S)-C(OH)(CH_2)_4$, m. $172-4^\circ$; $[Me_2C(CCl_3)O]_2P(S)C(OH)(CH_2)_5$, m. $181-3^\circ$; $[(CH_2)_4C(CCl_3)O]_2P(S)CHPhOH$, m. $142-3^\circ$; $[(CH_2)_4C(CCl_3)O]_2P(S)CH(OH)C_6H_4NO_2$, m. $157-3^\circ$; $[(CH_2)_4C(CCl_3)O]_2P(S)CHMe_2OH$, m. $162-3^\circ$; $[(CH_2)_4C(CCl_3)O]_2P(S)-C(OH)(CH_2)_5$, m. $158-60^\circ$. Products with AcH , $EtCHO$, $BuCHO$, $isobuCHO$, $ClCH_2Ac$ and $p-O_2NC_6H_4CHO$ failed to crystallize and were not purifiable. Salicylaldehyde gave a red glassy product. Neither $EtONa$ nor Et_3N appear to catalyze this addn. Treatment of X with $N NaOH$ results in cleavage and formation of RuH even at 30° ; the reaction is rapid at 50° .

*reanalysis***Mechanism of the Arbuzov rearrangement.**

A. I. Razumov (Chem. Technol. Inst., Kazan). Zhur. Obshchei Khim. 29, 1635-9 (1959).

The Arbuzov rearrangement is examined from the viewpoint of accelerating effect exerted by the increasing electron density at the P atom of the P^{III} ester involved in the reaction. It was shown by dilatometric studies that the reaction rate increases rapidly with replacement of RO groups by R groups. Thus $(EtO)_3P$ and EtX (the phosphite having been prepd. in the presence of a tert. amine) react completely in 1185 min. at 100.4° and in 650 min. at 110° (temp. coeff. 1.87); $EtP(OEt)_2$ and EtX react in 540 min. at 64.5° or 240 min. at 72.1° , while Et_2POEt and EtX react in 345 min. at 45° or 120 min. at 55° . The temp. coeff. for the 2nd reaction is 2.9 and for the 3rd it is 2.87. Reducing these reaction times to those expected for 100° , the following calcd. reaction times are found $(EtO)_3P$ 1214 min., $EtP(OEt)_2$ 12, Et_2POEt 1. $(EtO)_3P$ prepd. from $EtONa$ required 5 hrs. 40 min. for reaction at 110° , while that prepd. with a tert. amine required 10 hrs. 50 min. 32 references are cited in the discussion.

organophosphorus
New method of synthesis of esters of phosphonic and thiophosphonic acids.

XXX. Reaction of dialkyl hydrogen phosphites and thiophosphites with ketones.

V. I. Nikitina and A. N. Pudevikh (State Univ., Kazan). Zhur. Obshchei Khim. 29, 1219-22(1959), cf. 25, 1369(1955).

Passage of excess CH_3CO into 25-30 g. $(\text{RO})_2\text{PHO}$ (or 5-10 g. $(\text{RO})_2\text{PSH}$) in 50-75 ml. CCl_4 and a few drops of pyridine or H_2SO_4 at $35-40^\circ$ (Et_2O may be used as the solvent instead of CCl_4) gave predominantly $\text{CH}_3\text{C}(\text{OAc})\text{P}(\text{O})-(\text{OR})_2$ (I) and much smaller amt. of $\text{AcP}(\text{O})(\text{OR})_2$ (II). The following are reported (R shown): II, Me, 5%, b_{16} $93-5^\circ$, n_D^{20} 1.4300, d_{20} 1.2102; I, Me, 68%, b_{11} $129.5-30^\circ$, 1.4390, 1.2170; II, Et, 5.6%, b_{13} $103-5^\circ$, 1.4209, 1.1005; I, Et, 71%, b_{13} $135-5.5^\circ$, 1.4375, 1.1347; II, Bu, 2.5%, b_{13} $128-30^\circ$, 1.4300, 1.0190; I, Bu, b_{10} $161-2^\circ$, 1.4420, 1.0613; II, iso-Bu, 3%, b_{14} $119-20^\circ$, 1.4280, 1.0015; I, iso-Bu 75%, b_{12} $152-3^\circ$, 1.4362, 1.0373; Similarly were obtained $\text{CH}_3\text{C}(\text{OAc})\text{P}(\text{S})(\text{OR})_2$: II, Me, 40%, b_{13} $121-2^\circ$, 1.4825, 1.2104; Et, 42%, b_{11} $126-8^\circ$, 1.4680, 1.1266; iso-Bu, 58%, b_{11} $153-4^\circ$, 1.4590, 1.041. Ozonolysis of I, Me gave CH_3O . Passage of CH_3CO into II, Et, in Et_2O in the presence of 2 drops pyridine at $35-40^\circ$ gave a moderate yield of I, Et. cf. Kennedy et al. C. A. (1957), 4933^o.

Reaction of dialkyl hydrogen phosphites with aldehydes and ketones. XIX.

Hi-1-trichloromethylcyclopentyl esters of α -hydroxyalkylphosphonic acids.

V. S. Abramov and V. K. Khairullin (Chem. Tech. Inst., Kazan). Zhur. Obshchei Khim. 29, 1222-5 (1959), cf. 23, 3059(1958).

Keeping equimolar mixt. of carbonyl compds. with $[(\text{CH}_2)_4\text{CCl}_3\text{O}]_2\text{PHO}$ (undistillable oil, n_D^{20} 1.5235, d_{20} 1.4770; prepd. from the chloride and H_2O ; cf. Trudy Kazan. Khim. Tekh. Inst. 23, 65(1957)) in ampul a few hrs. gave the following $[(\text{CH}_2)_4\text{CCl}_3\text{O}]_2\text{P}(\text{O})\text{C}(\text{OH})\text{RR}'$ (R, R' shown resp.): H, Me, 82.5%, n $143-5^\circ$; H, Et, 74.5%, n $156.5-7.5^\circ$; H, Pr, 74%, n $136-7^\circ$; H, iso-Bu n $155-7^\circ$, 55.6%; H, CCl_3 , n $163-4^\circ$, 82%; H, Ph, 92%, n $143-4^\circ$; H, $p\text{-MeC}_6\text{H}_4$, 91.3%, n 162° ; $m\text{-O}_2\text{NC}_6\text{H}_4$, 77%, n $156-7^\circ$; H, $o\text{-NOC}_6\text{H}_4$, 90%, n $149-50^\circ$; $(\text{CH}_2)_3$, 92%, n $179-80^\circ$.

Some esters of ethylvinyl- and ethylallylphosphinic acids.

G. Kamai and V. S. Tsivunin (B.M.Kirov Chem. Technol. Inst., Kazan). Doklady Akad. Nauk S.S.S.R. 128, 543-6 (1959). Cf. Zhur. Obsh.Khim.25,1932(1958).
 Passage of ethylene oxide into 20 g. EtPCl_2 in abs. Et_2O with cooling at $15-30^\circ$ and using N_2 for inert atm. resulted in 27 g. $\text{EtPClOCH}_2\text{CH}_2\text{Cl}$, b_5 46° , n_D^{20} 1.4560, d_{20} 1.2200 or $\text{EtP}(\text{OCH}_2\text{CH}_2\text{Cl})_2$, b_5 92° , 1.4795, 1.2030, depending on the relative proportion of reactants used. The latter ester is slowly oxidized in air and reacts with S and CuCl . Heating this ester in EtPh at $138-40^\circ$ under N_2 1 hr. gave $\text{ClCH}_2\text{CH}_2\text{P}(\text{O})\text{Et}(\text{OCH}_2\text{CH}_2\text{Cl})$, b_4 $132-4^\circ$, 1.4652, 1.2690. This (25 g.) added to 24 g. PCl_5 suspended in Et_2O at $5-15^\circ$ gave 11 g. $\text{ClCH}_2\text{CH}_2\text{P}(\text{O})\text{EtCl}$, b_{10} 127° , 1.4900, 1.2985. This (120 g.) was passed over 0.5 hr. through a quartz tube packed with calcined BaCO_3 at $300-30^\circ$ and yielded 70 g. $\text{CH}_2=\text{CHP}(\text{O})\text{EtCl}$, b_{10} 90° , 1.4805, 1.1695. The above chlorides were treated with various alcoh. in the presence of pyridine in Et_2O preferably at -5° to 5° , yielding 60-80% following esters: $\text{ClCH}_2\text{CH}_2\text{P}(\text{O})\text{Et}(\text{OEt})$, b_3 $86-8^\circ$, 1.4584, 1.1300; $\text{CH}_2=\text{CHP}(\text{O})\text{Et}(\text{OEt})$, b_{11} 80° , 1.4518, 1.0500; Et ester, b_{14} 86.5° , 1.4495, 1.0210; Pr ester, b_{10} $94-5^\circ$, 1.4468, 0.9851; iso-Pr ester, b_{10} 83° , 1.4440, 0.9777; allyl ester, b_{10} $99-100^\circ$, 1.4640, 1.0160; Bu ester, b_{10} 106° , 1.4472, 0.9716; iso-Bu ester, b_{10} $99-100^\circ$, 1.4448, 0.9674; iso-Am ester, b_{10} 112° , 1.4466, 0.9561. The chloride and ethylene oxide gave 50% $\text{CH}_2=\text{CHP}(\text{O})\text{Et}(\text{OCH}_2\text{CH}_2\text{Cl})$, b_7 107° , 1.4695, 1.1610. Reaction of $\text{EtP}(\text{OR})_2$ with $\text{CH}_2=\text{CHCH}_2\text{Br}$ gave: 70% $\text{CH}_2=\text{CHCH}_2\text{P}(\text{O})\text{Et}(\text{OEt})$, b_{12} $115-7^\circ$, 1.4672, 1.0100; 50% Pr ester, b_{10} $111-2.5^\circ$, 1.4480, 0.9792; 20% iso-Pr ester, b_{10} $98-9^\circ$, 1.4450, 0.9701, 35% Bu ester, b_{10} $120-2^\circ$, 1.4495, 0.9670; 40% iso-Bu ester, b_{10} $116-8^\circ$, 1.4476, 0.9596; 45% iso-Am ester, b_{10} $129-38^\circ$, 1.4495, 0.9506. The esters of unsatd. phosphinic acids were polymerized with 2% $\text{K}_2\text{S}_2\text{O}_8$ at $80-120^\circ$. Esters with the vinyl group polymerized to gels in 20-40 hrs. with the allyl ester being polymerized to a waxy solid in 4 hrs. Among esters of ethylallylphosphinic acid, the allyl ester (I) polymerized to a waxy solid in 3 hrs. while the others failed to polymerize in 6 days.

*organo-phos***Synthesis of triallyl phosphate.**

B. V. Kuznetsov and R. K. Valotdinov (S.M.Kirov Chem. Tech. Inst., Kazan).
 Zhur. Obshchei Khim. 29, 2017-8 (1959). cf. USPat 2,394,829, C.A. 40, 2564
 (1946).

To 261 g. $\text{CH}_2=\text{CHCH}_2\text{OH}$, 356 g. pyridine and 1 l. Et_2O was added at $0-5^\circ$
 206 g. PCl_3 in 250 ml. Et_2O ; filtration and distn. gave 190 g. $(\text{CH}_2=\text{CHCH}_2\text{O})_3\text{P}$,
 b_{11} $89-93^\circ$, n_D^{20} 1.4560 (cf. V.M. Leroastreva, Dissertation, Kazan (1945),
 b_9 $85.5-86.5^\circ$, n_D^{18} 1.4595, d_4^{20} 0.9974). This (150 g.) heated on a CCl_4 bath
 was treated with a stream of dry O_2 6 hrs. yielding on distn. which occurs
 without any sign of decompn. 83% $(\text{CH}_2=\text{CHCH}_2\text{O})_3\text{PO}$, b_1 $93-4^\circ$, d_{20} 1.0815,
 n_D^{20} 1.4500. The reaction was followed by change in n .

Preparation and isomerization of mixed esters of bis- β,β' -dichloroisopropyl hydrogen phosphite.

V. K. Khairullin, A. I. Ledeneva and V. S. Abramov (Chem. Tech. Inst., Kazan). Zhur. Obshchei Khim. 29, 2355-9 (1959). cf. 27, 2381 (1957).

Addn. of 258 g. $\text{HOCH}(\text{CH}_2\text{Cl})_2$ to 274.7 g. PCl_3 over 3 hrs. and stirring 1.5 hrs. longer, followed by removal of HCl in vacuo, gave a range of fractions from which was obtained: a) 22% $(\text{ClCH}_2)_2\text{CHOPCl}_2$ ^(I), b_2 75°, d_{20} 1.4973, n_D^{20} 1.5195, b) 25.4% $[(\text{ClCH}_2)_2\text{CHO}]_2\text{PCl}$ ^(II), b_1 135-7°, 1.4903, 1.5189, and c) 9.8% $[(\text{ClCH}_2)_2\text{CHO}]_2\text{P}(\text{O})\text{CH}_2\text{CHClCH}_2\text{Cl}$, b_2 208-10°, 1.5018, 1.5130.

The last fraction, 63 g., b_2 139-208°, appeared to contain $(\text{RO})_2\text{P}$ since it reacted exothermically with CuCl , but attempts to isolate the neutral phosphite in the pure state were unsuccessful. Reaction of I with various alcoh. in the presence of pyridine gave $(\text{ClCH}_2)_2\text{CHOP}(\text{OR})_2$ (R shown): Me, 47.5%, b_4 84°, 1.2375, 1.4680; Et, 65%, $b_{1.5}$ 84-6°, 1.1890, 1.4605; Pr, 51%, b_2 105-7°, 1.1393, 1.4585; Bu, 53%, b_1 122-4°, 1.1990, 1.4550.

Heating the di-Et ester with EtI 1.5 hrs. at 100° gave 50% $\text{EtP}(\text{O})(\text{OEt})\text{OCH}(\text{CH}_2\text{Cl})_2$, b_1 100°, 1.2470, 1.4610. Similarly the di-Bu ester and BuI in 19 hrs. at 100° gave 66.7% $\text{BuP}(\text{O})(\text{OBu})\text{OCH}(\text{CH}_2\text{Cl})_2$, $b_{1.5}$ 140-2°, 1.1326, 1.4585. Treatment of 98.85 g. I in Et_2O with 15.5 ml. H_2O at 0° gave ^(III) After evapn. in vacuo an oily residue of $(\text{ClCH}_2)_2\text{CHOP}(\text{O})\text{H}_2$. Condensation of this acid or $\text{RP}(\text{O})(\text{OR})\text{OCH}(\text{CH}_2\text{Cl})_2$ with Ca polysulfide gave yellow

powdery polymers which were insol. in the usual solvents. The reaction of I with alcoh. invariably gave a range of products, besides the esters listed above; it is suggested that this occurred owing to the disproportionation of the alkoxy groups on the P atom during fractionation.

II and H_2O gave the corresponding $(\text{RO})_2\text{PHO}$ which was not described; this is capable of adding to aldehydes and ketones. III purified by careful evacuation of volatiles, is an oil, d_{20} 1.5040, n_D^{20} 1.4866.

Reaction

Reaction of dialkyl hydrogen phosphites with aldehydes and ketones. XXI.
Di- β,β' -dichloroisopropyl esters of substituted α -hydroxymethylphosphonic acid.

V. K. Khairullin, A. I. Ledeneva and V. D. Abramov (Chem. Technol. Inst., Kazan). Zhur. Obshchei Khim. 29, 2551-3 (1959). cf. 27, 2387 (1957). and Trudy Kazan. Khim. Tekhnol. Inst. im. S. M. Kirova, 23, 103 (1957).

To 72.1 g. $((\text{ClCH}_2)_2\text{CHO})_2\text{PCl}$ was added 4 g. H_2O with ice-salt cooling below 0° ; evapn. of the mixt. in vacuo gave 96.5% liquid $[(\text{ClCH}_2)_2\text{CHO}]_2\text{PNO}$, $d_{20} 1.4917$, $n_D^{20} 1.4976$. This kept at room temp. with equimolar amounts of aldehydes and ketones 1-20 days gave the following $[(\text{ClCH}_2)_2\text{CHO}]_2\text{P(O)R}$ (R shown): CCl_3CHOH , m. $110-2^\circ$, 71%; PhCHOH , m. $80.5-1.5^\circ$, 67%; $m\text{-O}_2\text{NC}_6\text{H}_4\text{-CHOH}$, m. $120-1^\circ$, 55%; Me_2COH , m. $79-80^\circ$, 60%; $(\text{CH}_2)_5\text{COH}$, m. $89-91^\circ$, 68%; EtCH_2COH also were prepd.: 41% $[(\text{CCl}_3\text{CMe}_2\text{O})]_2\text{P(O)CMe(OH)CH}_2\text{Cl}$, m. 151° , 41%; $[(\text{CCl}_3\text{CMe}_2\text{O})]_2\text{P(O)C(OH)(CH}_2\text{Cl)}_2$, m. $176-7^\circ$, 74%. The products with AcH , EtCHO , PrCHO and iso-BuCHO were liquids and failed to crystallize.

Organic insectofungicides. XLII. Synthesis of some mixed esters of dithiophosphoric acid.

N. N. Mel'nikov, K. D. Shvetsova-Shilovskaya, M. Ya. Kagan and I. M. Mil'shtein (Fertiliz. Insectofung. Res. Inst., Moscow). Zhur. Obshchei Khim. 29, 1612-4 (1959). cf. 23, 1357 (1955).

Refluxing $(RO)_2PS_2K$ in Me_2CO or $EtOH$ with appropriate halide (substituted benzyl chloride or 1-aryl-3-bromopropane) 2.5-3 hrs. gave, after washing the crude product in C_6H_6 with H_2O , the following products for tests as potential insecticides: $(RO)_2PS_2R'$ (R and R' shown resp.):
 Me, $PhCH_2$, 53%, $b_{0.11}$ 117-7.5°, d_{20} 1.2217, n_D^{20} 1.5818; Et, $PhCH_2$, 50%, $b_{0.07}$ 112-2.5°, 1.1571, 1.5600; Pr, $PhCH_2$, 80%, $b_{0.12}$ 132-3°, 1.1058, 1.5461; iso-Pr, $PhCH_2$, 66%, $b_{0.12}$ 118-20°, 1.1103, 1.5432; Bu, $PhCH_2$, 77%, $b_{0.1}$ 136-8°, 1.0849, 1.5390; Me, $p-ClC_6H_4CH_2$, 42%, $b_{0.16}$ 133-5°, 1.3046, 1.5897; Et, $p-ClC_6H_4CH_2$, 60%, $b_{0.35}$ 138-40°, 1.2278, 1.5675; Pr, $p-ClC_6H_4CH_2$, 63%, $b_{0.1}$ 137-8°, 1.1739, 1.5560; iso-Pr, $p-ClC_6H_4CH_2$, 53%, $b_{0.2}$ 138.5-40°, 1.1745, 1.5518; Bu, $p-ClC_6H_4CH_2$, 61%, $b_{0.09}$ 154-5°, 1.1378, 1.5460; Me, $p-O_2NC_6H_4CH_2$, 71%, undistillable; Et, $p-O_2NC_6H_4CH_2$, 47%, $b_{0.1}$ 168-74°, 1.2807, 1.5775; iso-Pr, $p-O_2NC_6H_4CH_2$, 79%, undistillable; Me, $Ph(CH_2)_3$, 25%, $b_{0.1}$ 139-40°, 1.1712, 1.5644; Et, $Ph(CH_2)_3$, 40%, $b_{0.1}$ 140-2°, 1.1240, 1.5472; iso-Pr, $Ph(CH_2)_3$, 60%, $b_{0.2}$ 149-51°, 1.0817, 1.5332; Me, $PhO(CH_2)_2$, 18%, $b_{0.28}$ 140-2°, 1.2408, 1.5698; Et, $PhO(CH_2)_2$, 41%, $b_{0.015}$ 152-4°, 1.1819, 1.5525; Pr, $PhOCH_2CH_2$, 58%, $b_{0.12}$ 145-6°, 1.1394, 1.5418; iso-Pr, $PhO(CH_2)_2$, 59%, $b_{0.3}$ 144-5°, 1.1264, 1.5365; Bu, $PhO(CH_2)_2$, 50%, $b_{0.12}$ 160-2°, 1.100, 1.5339.

*organophos***Esters of perfluoroalkenylphosphonic acids.**

I. L. Knunyants, B. Ya. Pervova and V. V. Tyuleneva (Inst. Hetero-org. pds., Moscow). Doklady Akad. Nauk S.S.S.R. 129, 576-7(1959). Cf. USP 2,559,-754 (C.A. 46, 1026 (1952)).

Heating 0.1 mole $(EtO)_3P$ and 0.3-0.4 mole perfluoro-olefin in an autoclave (10 hrs. at 5° for perfluorocyclobutene; 8 hrs. at 100° for perfluoroisobutylene, 8 hrs. at $130-40^\circ$ for perfluoropropylene and 8 hrs. at 170° in the presence of tertiary amine for perfluoroethylene) gave the following new products $RP(O)(OEt)_2$ (R shown): $CF_2=CF$, b_7 81° , d_{20} 1.260, n_D^{20} 1.377; $CF_3CF=CF$, b_8 83° , 1.312, 1.367; $(CF_3)_2C=CF$, b_8 85° , 1.400, 1.365; 1-perfluorocyclobutenyl, b_5 80° , 1.351, 1.392. This new reaction evidently involves the attack by the ~~xxx~~ nucleophilic $(RO)_3P$ on the positively polarized terminal C atom of the fluoro-olefin which contains 2 P bonds; alkyl fluoride is then eliminated from the intermediate adduct which is a bipolar ion. Some low boiling byproducts also form in the reaction. With C_2F_4 where the polarization of C is absent, the main product is $EtP(O)OEt)_2$ formed probably by isomerization of $(EtO)_3P$ by EtF , and only in the presence of a tertiary base which lowers the rate of such isomerization is it possible to obtain the fluorinated phosphonate in 10-15% yields. The yields of other esters range from 21% for the perfluorocyclobutenyl member to 66% for the perfluoroisobutylene member. The sepn. of the perfluorovinyl member from the Et byproduct was done by soln. of the latter in H_2O in which the former is insol.

Vinylphosphonic acid and some of its derivatives.

B. I. Sabachnik and T. Ya. Medved. (Inst. Hetero-org. Compds., Moscow).

Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 2142-5.

Passage of 45.4 g. $\text{ClCH}_2\text{CH}_2\text{POCl}_2$ through a tube packed with BaCl_2 at $330-40^\circ$ over 5 hrs. in N_2 stream gave 85.6% $\text{CH}_2=\text{CHPOCl}_2$ ^(I), b_{21} $67-9^\circ$, n_D^{20} 1.4808, d_{20} 1.4092; at lower temp. the yield is much lower. The dichloride and EtOH in the presence of pyridine in Et_2O at -4° gave 45% $\text{CH}_2=\text{CHPO}(\text{OEt})_2$, b_3 62° , 1.4338, 1.0550. This with Br_2 in CHCl_3 gave $(\text{EtO})_2\text{P}(\text{O})\text{CBr}:\text{CH}_2$, b_3 $88-90^\circ$, 1.4681, 1.4051; and a lesser amt. of $(\text{EtO})_2\text{P}(\text{O})\text{CHBrCH}_2\text{Br}$, b_3 $123-5^\circ$, 1.4943, 1.0595. I and ROH similarly gave: 44% $\text{CH}_2=\text{CHPO}(\text{OMe})_2$, b_{10} 72.5° , 1.4330, 1.0403; 16% $\text{CH}_2=\text{CHPO}(\text{OCMe}_2)_2$, b_5 $53-60^\circ$, 1.4269, 0.9908; 84% $\text{CH}_2=\text{CHPO}(\text{OPh})_2$, $b_{0.0004}$ $109.5-10^\circ$, 1.5571, 1.0930; 53% $\text{CH}_2=\text{CHPO}(\text{OCH}_2)_2\text{O}$, b_2 $129-30^\circ$, 1.4775, 1.0290. I added to H_2O with cooling gave on evapn. in vacuo over P_2O_5 a. KOH at 50° a sirupy $\text{CH}_2=\text{CHPO}_3\text{H}_2$, n_D^{20} 1.4777, d_{20} 1.0888. Distn. in high vacuum gave evidently an anhydride, $\text{O}(\text{P}(\text{O})(\text{OH})\text{CH}:\text{CH}_2)_2$, $b_{0.0006}$ $235-40^\circ$ 1.4651, 1.4622, a colorless sirup. I and Me_2NH in Et_2O gave 52% $\text{CH}_2=\text{CH}-\text{P}(\text{OMe})_2$, b_3 32° , 1.4733, 1.0657. Reactions of I with ROH are best run in the presence of NEt_3 in Et_2O .

of J. Am. Chem. Soc.

Imides of acids of phosphorus. Infrared absorption spectra of imido phosphates and imido phosphonates.

M. I. Kabachnik, V. A. Gilyarov and N. N. Tsvetkov (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 2135-41. cf. this J. 1956, 790 and Doklady Akad. Nauk SSSR 117, 817 (1957).

It was shown that the infrared absorption spectra of $(RO)_3P=NMe$ and $(RO)_2P(=O)NPh$ have a band at $1325-1385\text{ cm}^{-1}$ which is assignable to the P=N link in these compds. Addn. of PhN_3 to 9.1 g. $BuP(OBu)_2$ in Et_2O with ice cooling gave N_2 and after 2 hrs. the mixt. was distd. yielding 61.5% $(BuO)_2P(=O)NPh$, $b_p 131-2^\circ$, n_D^{20} 1.4990, d_{20} 0.9809. Similarly were prepd.: 66.7% $(BuO)_2P(=O)NPh$, $b_p 107.5-108^\circ$, 1.5050, 1.0066; 53% $(PrO)_2P(=O)NPh$, $b_p 102^\circ$, 1.5088, 1.0185; 66.3% $(BuO)_2P(=O)NPh$, $b_p 117-8^\circ$, 1.5045, 0.9955; 61.5% $(BuO)_2P(=O)NPh$, $b_p 123-4^\circ$, 1.5010, 0.9907; 85% $(BuO)_2(cyclo-C_5H_9)P(=O)NPh$, $b_p 148^\circ$, 1.5090, 1.0150; 54% $(EtO)_2P(=O)NPh$, $b_p 125^\circ$, 1.5708, 1.1083; 72% $(PrO)_2P(=O)NPh$, $b_p 127-9^\circ$, 1.5573, 1.0770. Distn. 2.86 g. $(BuO)_2P(=O)NPh$ with 0.53 g. $AcOH$ in C_6H_6 2 hrs. at 70° followed by distn. of $BuOAc$, gave $(BuO)_2P(=O)NPh$, $b_p 137^\circ$, 1.5100, 1.0036, in 60% yield. Treatment of 8 g. $(PrO)_3P$ with 4.1 g. MeN_3 in C_6H_6 at $12-17^\circ$ gave N_2 and a distn. on the following day yielded 50.8% $(PrO)_3P=NMe$, $b_p 82-5^\circ$, 1.4292, 0.9696; similarly were prepd. 50% $(EtO)_3P=NMe$, $b_p 70.5-1.5^\circ$, 1.4258, 1.0018, and 55% $(BuO)_3P=NMe$, $b_p 92.5-4^\circ$, 1.4380, 0.9497. These are readily hydrolyzed by H_2O yielding $(RO)_2P(=O)NHMe$. They react with CS_2 or before heated a few hrs. at 60° and yield $(RO)_3PS$ and $MeNCS$. Absorption spectra of the above products in the infrared are shown. The spectrum of $(EtO)_3P=NMe$ (prepd. from $(EtO)_3P$ and MeN_3) also shows a band at 1350 and 1385 cm^{-1} . The spectrum of $(EtO)_3P=NMe$ has a band at 1325 cm^{-1} which slowly decreases in intensity on standing in air, while the 1350 cm^{-1} band of the $P(=O)$ group increases in intensity.

Vibration spectra of organophosphorus compounds. The problem of the characterization of the P=S frequency.

E. M. Popov, T. A. Mastryukova, N. P. Rodionova and M. I. Kabachnik
(Inst. Hetero-org. Compds., Moscow). Zhur. Obshchei Khim. 29, 1998-2006(1959)
Cf. Doklady Akad. Nauk SSSR 104, 861(1955).

The existing literature on infrared and Raman spectra of organic compds. with a P=S group is reviewed (18 references). It is pointed out that previous workers have attempted to fix a characteristic frequency for P=S without regard for the effects of attached groups on such frequency, this effect being expectedly greater for P=S than for P=O group. Both types of spectra are reported for: EtOPSCl₂, EtOP(OC)Cl₂, MePSCl₂, PrPSCl₂, EtPOCl₂, (MeO)₂PSCl, (EtO)₂PSCl, (PrO)₂PSCl, (BuO)₂PSCl, (iso-PrO)₂PSCl, (MeO)₂PSNHMe, (EtO)₂PSNHMe, (PrO)₂PSNHMe, (BuO)₂PSNHMe, (iso-PrO)₂PSNHMe, Me₂NPSCl₂, Me₂NPOCl₂, MePS(OMe)Cl, MePSCl(OEt), MePS(OEt)₂, MePO(OEt)(SEt), EtPS(OEt)₂, EtPO(OEt)(SEt), (EtO)₂P(S)ONa, MePS(ONa)OEt, EtPS(ONa)OEt, [(EtO)₂PS]O₂P(OEt)₂, (EtO)₂PS₂H, (EtO)₂PO₂H, (EtO)₂PS₂Et, (EtO)₂P(S)SCH₂CH₂SEt, (EtO)₂PS₂CH₂SPr, (EtO)₂PS₂CH₂CH₂SPr. The P=S absorption band appears in these compds. in the region of 750-580 cm⁻¹ with variations caused by proximate groups. The following values are typical: PSCl₃ 750; ROPSCl₂ 700; (RO)₂PSCl 660; (RO)₃PS 610; RPOCl₂ 665; RPS(OR)Cl 620; RPS(OR)₂ 580; R₂NPSCl₂ 670; RNHPS(OR)₂ 640; (RO)₂PS₂H 650; (RO)₂(RS)PS 660; (RO)₂PS 630.

A method of preparation of dialkylthiophosphinic acids.

T. A. Mastryukova, A. E. Shipov and M. I. Kabachnik (Inst. Hetero-org. Compds., Moscow). Zhur. Obshchei Khim. 29, 1450-3 (1959).

Cf. A.E. Arbuzov, Sbornik Referatov VI Mendeleev. S'ezda, Kharkov, part II, 124 (1932); Kosolapoff and Watson, JACS 73, 4101 (1951).

It was shown that the addn. of S to the magnesium salt formed from the reaction of a Grignard reagent and $(RO)_2POH$ results in formation of dialkylthiophosphinic acids. Thus, Grignard reagent from 0.65 g.at. Mg and 0.69 mole RX in Et_2O , was treated under N_2 with 0.2 mole $(RO)_2POH$ at the rate that provided a refluxing of the solvent Et_2O ; after 1 hr. on a steam bath, the stirred mixt. was treated with 0.25 mole S (excess), the addn. causing an exothermic reaction. After 1 hr. on a steam bath, the cooled mixt. was treated with 1:1 HCl until the ppt. dissolved (the temp. is kept below 20° by external cooling), yielding a 3-layer mixture. Addn. of H_2O results in coalescence of 2 layers. The ethereal layer was sepa. and the aq. layer extd. with Et_2O ; the combined exts. were concd., treated with 100 ml. H_2O and adjusted to alkaline reaction to litmus with Na_2CO_3 . The insol. part was taken up in Et_2O while the aq. soln. was acidified with excess HCl and extd. with ~~hex~~ C_6H_6 . Distn. of the dried ext. gave 64-88% R_2PSOH . Either $(EtO)_2POH$ or $(BuO)_2POH$ may be used in the reaction. Thus were prepd. Et_2PSOH , $b_{1.5}$ $88.5-9^\circ$, n. 11.5° , n_D^{20} 1.5262, d_{20} 1.1090; Pr_2PSOH , b_2 $98.5-9^\circ$, n. 31° ; $iso-Pr_2PSOH$, n. $76-7.5^\circ$; Bu_2PSOH , $b_{0.025}$ $81-1.5^\circ$; $iso-Bu_2PSOH$, n. $69.5-70.5^\circ$; $(PhCH_2)_2PSOH$, n. $190.5-1.5^\circ$ (Strecker et al., Ber. 49, 63 (1916) give n. 171°). Reaction of $(BuO)_2PCl$ with $PrMgBr$ (cf. Doklady Akad. Nauk SSSR, 117, 817 (1957)) gave $PrP(OBu)_2$, b_7 $93.5-5^\circ$, n_D^{20} 1.4400, d_{20} 0.8844 (70%), which with $PrBr$ in 3 hrs. at 160° gave 80.8% $Pr_2P(O)OBu$, b_1 $78-9^\circ$, 1.4339, 0.9143, which with PCl_5 gave 81% Pr_2POCl , b_3 $110.5-12^\circ$, 1.4662, 1.0689, which heated with P_2S_5 2 hrs. at $130-50^\circ$ gave 59% Pr_2PSCl , b_7 $107-9^\circ$, 1.5190, 1.0315. This (10 g.) heated 1.5 hrs. under N_2 with 6.17 g. KOH in 100 ml. 70% $EtOH$ gave after an ac.

treatment, removal of neutral products with Et_2O , acidification and extn. with C_6H_6 gave a soln. of Pr_2PSOH which after drying with Na_2SO_4 was treated with dry NH_3 yielding the NH_4 salt, 54%, m. $116.5-8.5^\circ$. Similarly, pure acid treated in petr. ether with NH_3 gave 96% above salt, m. $117-9^\circ$. The Reaction of EtMgBr from 38 g. EtBr with 8 g. PCl_3 in Et_2O gave after treatment with 1:1 ice- HCl , extn. of the aq. layer with Et_2O and evapn. of the combined dried ethereal exts., a solid residue of $(\text{Et}_2\text{Pz})_2$, m. $76-7^\circ$. The substance does not titrate with NaOH in the cold but does dissolve in hot 20% NaOH . This substance was assumed to be Et_2PSOH by Strecker et al.

Organophosphorus insecticides. VI. Amide esters of thiophosphoric phosphoric acids containing the β -ethylmercaptoethyl grouping.

M. T. Kabachnik, M. N. Godovikov, D. M. Paikin, N. P. Shabanova, L. P. Efimova and N. E. Gampor (Inst. Hetero-org. Compds., Moscow), Zhur. Obshchei Khim. 29, 2182-90 (1959).

The following were prepd. for insecticidal studies. Passage of Me_2NH into EtOPSCl_2 in Et_2O at -5° , followed by stirring 1 hr. at room temp. gave after filtration 79% $\text{EtOPS}(\text{NMe}_2)\text{Cl}$, b_3 $72-3^\circ$, n_D^{20} 1.4972, d_{20} 1.2008. Similarly was prepd. 48% $\text{EtOPS}(\text{NEt}_2)\text{Cl}$, b_{10} $105-6^\circ$, 1.4931, 1.1352. PSCl_3 and 4 moles Me_2NH at first at $0-5^\circ$, finally at room temp. in Et_2O gave 56% $(\text{Me}_2\text{N})_2\text{PSCl}$, b_1 $57-8^\circ$, n_D^{23} 1.5229, $n. 22^\circ$ (from petr. ether); the same formed in 43% yield by heating 26 g. $(\text{Me}_2\text{N})_2\text{POCl}$ and 3.5 g. P_2S_5 under N_2 5 hrs. at $150-60^\circ$. Heating 600 g. 40% HBr , 106 g. $\text{EtSCH}_2\text{CH}_2\text{OH}$ and 76 g. $\text{CS}(\text{NH}_2)_2$ 10 hrs. at reflux, followed by addn. of 120 g. NaOH in 300 ml. H_2O and heating 3 hrs., gave after extn. with Et_2O 66% $\text{EtSCH}_2\text{CH}_2\text{SH}$, b_{13} $69-70^\circ$, n_D^{20} 1.5281, d_{20} 1.0381. Stirring 4 g. powd. NaOH and 10.6 g. $\text{EtSCH}_2\text{CH}_2\text{OH}$ 15 min., then adding 150 ml. C_6H_6 , followed by 18.7 g. $(\text{Me}_2\text{N})(\text{EtO})\text{PSCl}$ at 15° , and heating 1 hr. at 70° gave 49% $(\text{EtO})(\text{Me}_2\text{N})\text{PS}(\text{OCH}_2\text{CH}_2\text{SEt})$, $b_{2.5}$ $112-4^\circ$, 1.5015, 1.1091; similarly was prepd. 24% $(\text{EtO})(\text{Et}_2\text{N})\text{PS}(\text{OCH}_2\text{CH}_2\text{SEt})$, b_2 $118-20^\circ$, 1.4972, 1.0779; and 50% $(\text{Me}_2\text{N})_2\text{PS}(\text{OCH}_2\text{CH}_2\text{SEt})$, $b_{1.5}$ $105-6^\circ$, 1.5151, 1.1008. Heating I under N_2 10 hrs. at $150-60^\circ$ (n variation ceased) gave 64% $(\text{EtO})(\text{Me}_2\text{N})\text{PO}(\text{SCH}_2\text{CH}_2\text{SEt})$, $b_{2.5}$ $122-3^\circ$, 1.5100, 1.1272; similarly were prepd.: $(\text{EtO})(\text{Et}_2\text{N})\text{PO}(\text{SCH}_2\text{CH}_2\text{SEt})$, b_3 $142-3^\circ$, 1.5046, 1.0884; and 61% $(\text{Me}_2\text{N})_2\text{PO}(\text{SCH}_2\text{CH}_2\text{SEt})$, b_1 $103-4^\circ$, 1.5208, 1.1165. To MeONa from 2.3 g. Na in 50 ml. MeOH was added 12.2 g. $\text{EtSCH}_2\text{CH}_2\text{SH}$, MeOH was distd. and replaced by C_6H_6 and 18.7 g. $(\text{EtO})(\text{Me}_2\text{N})\text{PSCl}$ was added and heated 1 hr. at 70° ; after an aq. treatment there was obtained 42% $(\text{EtO})(\text{Me}_2\text{N})\text{PS}_2\text{CH}_2\text{CH}_2\text{SEt}$, $b_{2.5}$ $136-7^\circ$, 1.5501, 1.1409; similarly was prepd. 32% $(\text{EtO})(\text{Et}_2\text{N})\text{PS}_2\text{CH}_2\text{CH}_2\text{SEt}$, b_2 $133-4^\circ$, 1.5430, 1.1113. The products were all decidedly less active against *Pseudococcus maritimus* than Parathion; in tests with *Eurygaster integriceps* the last compd. was comparable to Parathion.

Application of the Hammett equation to ionization constants of organophosphorus acids in 7% and 80% alcohol.

T. A. Mastryukova, T. A. Molent'eva, A. E. Shipov and K. I. Kabachnik (Inst. Hetero-org. Compds., Moscow). Zhur. Obshchei Khim. 29, 2178-82 (1959).

cf. Doklady Akad. Nauk SSSR 110, 393 (1956).

The following ionization constants were detd. by pH measurements of partly neutralized solns. of the acids without correction for activity change in passing from H₂O to 80% EtOH: (MeO)₂PO₂H in 7% EtOH pK₁ 1.25, in 80% EtOH pK₁ 3.01; (EtO)₂PO₂H 1.37 and 3.15; (PrO)₂PO₂H 1.52 and 3.29; PhOPO(OH)₂ pK₁ 1.46, pK₂ 6.29, and pK₁ 3.36, pK₂ 8.71; (PhO)₂PO₂H -, 2.71; p-MeC₆H₄OPO(OH)₂, 1.64, 6.45, and 3.45, 8.81; (p-MeC₆H₄O)₂PO₂H 1.36 and 2.91; Me₂PO₂H, 3.13 and 5.15; Bu₂PO₂H 3.50 and 5.63; (iso-Bu)₂PO₂H 3.70 and 5.63; (p-ClC₆H₄)₂PO₂H 1.68 and 3.48; Ph₂PO₂H 2.32 and 4.24; (p-MeC₆H₄)₂PO₂H 2.47 and 4.45; (m-O₂NC₆H₄)₂PO₂H -, and 2.37. The Hammett σ values for the aryloxy groups at a P atom were found to be -0.073 (average) for PhO, and -0.116 (average) for p-MeC₆H₄O group, as calcd. from the pK data. Plotting pK as a function of σ in 7% and 80% EtOH gave the probable mean value of σ for PhO -0.061 and for p-MeC₆H₄O -0.141, which compare favorably with the above values calcd. from data in 50% EtOH (PhOPO₃H₂ pK 2.61; PhOPO(OH)O⁻ pK 7.66; (PhO)₂PO₂H pK 2.28; p-MeC₆H₄OPO₃H₂ pK 2.69; p-MeC₆H₄OPO(OH)O⁻ pK 7.74; (p-MeC₆H₄O)₂PO₂H pK 2.32). From data on pK values of phosphonic and phosphinic acids it was calcd. that σ for Ph is -0.481 and p-MeC₆H₄ is -0.602; although the results of use of these values were satisfactory for RPO₃H₂, they were not satisfactory for R₂PO₂H. Detn. of pK of Ph₂PO₂H in 50% EtOH gave the value of 3.43 and that for (p-MeC₆H₄)₂PO₂H was found to be 3.66; this gave the value of Ph -0.542 and -0.629; calcn. of these σ values graphically from data in aq. alc. media gave the more probable values of -0.592 and -0.674, resp. These values must be used for Hammett equation for R₂PO₂H, i.e. the number of R groups at the P atom affects the actual value of σ , probably through steric effects. The reference compd. for the use of Hammett equation

was H_3PO_2 . The values of pK_0 and σ for the ionization constants of P acids were estd. at 1.01 and 1.050, resp., for 7% EtOH and 2.68 and 1.219 for 80% EtOH. Plots of $\text{pK}-\text{pK}_0 - \sigma$ for these two media for 14 compds. showed good straight line relationship for each medium. The following new data are also reported: $(\text{p-MeC}_6\text{H}_4\text{O})_2\text{PO}_2\text{H}$, m. 80.5-1.5°; $(\text{p-MeC}_6\text{H}_4)_2\text{PO}_2\text{H}$, m. 132-3°; $(\text{m-O}_2\text{NC}_6\text{H}_4)_2\text{PO}_2\text{H}$, m. 270-1°. It is pointed out that in the 1st paper (cf. ref. above) the following σ values were reported erroneously: for iso-Pr should be -1.300 instead of -0.300, and for Bu group should be -1.219 instead of -0.219.

Reaction of phosphorus pentachloride with dichlorides and diesters of arylsulfonamidophosphoric acids.

E. S. Levchenko, I. N. Zhmurova and A. V. Kirsanov (Inst. Org. Chem., Acad. Sci., Kiev). Zhur. Obshchei Khim. 29, 2262-7 (1959). cf. this J. 29, 2256(1959).

Reaction of PCl_5 with $\text{ArSO}_2\text{NHPOCl}_2$ results in formation of $\text{ArSO}_2\text{N:PCl}_3$. Refluxing 0.02 mole $\text{ArSO}_2\text{NHPOCl}_2$ with 0.0315 mole PCl_5 in 5 ml. CCl_4 30-40 min. until HCl evolution ceased, was followed by evapn. of the solvent in vacuo at $80-90^\circ$, yielding a largely cryst. ~~xxix~~ residue contg. a little liquid which was removed with a small vol. of Et_2O ; in this manner were prepd. 51% $\text{ArSO}_2\text{N:PCl}_3$, $\text{Ar} = o\text{-O}_2\text{NC}_6\text{H}_4$, m. $69-71^\circ$; 47% m -isomer, m. $72-3^\circ$; 57% p -isomer, m. $115-7^\circ$. The reaction may be run without a solvent at $130-5^\circ$ 10-15 min. Heating 0.02 mole $p\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NHPOCl}_2$ (cf. this J. 27, 3078(1957)) with 0.021 mole PCl_5 15-20 min. at $130-5^\circ$ until HCl evolution ceased, was followed by evapn. in vacuo and extn. with C_6H_6 ; the filtered ext. on evapn. in vacuo gave 57% $p\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{N:PCl}_3$, m. $115-7^\circ$. Reaction of 0.011 mole PCl_5 with 0.01 mole $p\text{-PhO}_3\text{SC}_6\text{H}_4\text{SO}_2\text{NHPOCl}_2$ (cf. ref. above) 20-5 min. at $115-20^\circ$ gave similarly 49% $p\text{-PhO}_3\text{SC}_6\text{H}_4\text{SO}_2\text{N:PCl}_3$, m. $103-4^\circ$. Reaction of equimolar amts. of PhONa and $\text{ClO}_2\text{SC}_6\text{H}_4\text{SO}_2\text{NH}_2\text{-p}$ in dioxane gave after an aq. treatment 61% $p\text{-PhO}_3\text{SC}_6\text{H}_4\text{SO}_2\text{NH}_2$, m. $173-4^\circ$ (from EtOH), which heated with 1.1 mole PCl_5 at 120° 0.5 hr. gave $p\text{-PhO}_3\text{SC}_6\text{H}_4\text{SO}_2\text{N:PCl}_3$, m. $103-4^\circ$ (from CCl_4). This with equimolar amt. of HCO_2H in dry C_6H_6 gave in 4 hrs. 84% $p\text{-PhO}_3\text{SC}_6\text{H}_4\text{SO}_2\text{NHPOCl}_2$, m. $158-60^\circ$ (from C_6H_6). Heating equimolar mixts. of PCl_5 and $\text{ArSO}_2\text{NHPO}(\text{OPh})_2$ 30-40 min. at $100-10^\circ$ gave after removal of the resulting POCl_3 in vacuo, the following $p\text{-(PhO)}_2\text{PCl:NSO}_2\text{Ar}$ (Ar shown): Ph, 51%, m. $71-3^\circ$; $p\text{-ClC}_6\text{H}_4$, 77%, m. $91-3^\circ$; $o\text{-O}_2\text{NC}_6\text{H}_4$, 84%, m. $64-5^\circ$; m -isomer, 80%, m. $82-4^\circ$; p -isomer, 91%, m. $79-81^\circ$. These with PhONa in C_6H_6 gave $(\text{PhO})_3\text{P:NSO}_2\text{Ar}$ (Ph, 87%, m. $85-6^\circ$; $p\text{-ClC}_6\text{H}_4$, 78%, m. $77-9^\circ$; o -

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$\text{O}_2\text{NC}_6\text{H}_4$, 96%, m. $78-9^\circ$; m-isomer, 98%, m. $102-4^\circ$. Reaction of p- $\text{ClC}_6\text{H}_4\text{SO}_2\text{N:PCl}_3$ with 3 moles PhONa in C_6H_6 gave after an aq. treatment of the reaction mixt. 87% p- $\text{ClC}_6\text{H}_4\text{SO}_2\text{N:P(OPh)}_3$, m. $78-80^\circ$ (from C_6H_6 -petr.ether). Treatment of p- $\text{ClC}_6\text{H}_4\text{SO}_2\text{NHPOCl}_2$ with 3 moles PhONa in dioxane gave after an aq. treatment, sepn. of the pptd. Na salt of the desired product and treatment of this with 5N HCl gave 90% p- $\text{ClC}_6\text{H}_4\text{SO}_2\text{NHPO(OPh)}_2$, m. $168-70^\circ$ (from EtOH). The reaction of PCl_5 with $\text{ArSO}_2\text{NHPOCl}_2$ takes place only if the Ar group contains an electronog. component; reactions with Ph, tolyl or chlorophenyl aryl groups failed to take place.

Extending the limits of application of the phosphazo reaction.

I. N. Zhmurov and A. V. Kirsanov (Inst. Org. Chem., Acad. Sci., Kiev).

Zhur. Obshchei Khim. 29, 1687-94 (1959). cf. 28, 1227 (1958).

The phosphorus-bearing component of the phosphazo reaction may be not only PCl_5 but $(\text{PhO})_5\text{P}$ or $(\text{PhO})_3\text{PCl}_2$. To 0.1 mole $(\text{PhO})_3\text{P}$ there was added 0.1 mole PCl_5 (exothermic) and after 5-10 min. a clear soln. was formed; this was heated in vacuo to 100° and finally to $130-40^\circ$ to remove PCl_3 , while the residue kept in a desiccator solidified after 1 day, yielding 100% $(\text{PhO})_3\text{PCl}_2$, m. $76-8^\circ$ (in sealed capillary). This (0.1 mole) and 0.2 mole PhOH heated 2 hrs. at $140-50^\circ$, then 2-3 hrs. at $150-60^\circ$ in vacuo until all HCl had been removed, gave after 1 day in a desiccator $(\text{PhO})_5\text{P}$, dec. $80-90^\circ$. (cf. Anschütz, Ann. 454, 77 (1927), who gives m. $46-52^\circ$). Heating 0.1 mole $(\text{PhO})_3\text{PCl}_2$ with 0.3 mole PhNH_2 at $120-30^\circ$ 2 hrs. gave after treatment with C_6H_6 , filtration and distn. $(\text{PhO})_3\text{P:NPh}$, b_g $254-7^\circ$. Heating 0.1 mole $(\text{PhO})_5\text{P}$ and 0.1 mole PhNH_2 2 hrs. at $140-50^\circ$, then 1 hr. in vacuo at 180° , gave 77% $(\text{PhO})_3\text{P:NPh}$, b_g $254-7^\circ$; the same formed from $(\text{PhO})_3\text{P}$ and PhN_3 in Et_2O , in 80% yield. Heating $(\text{PhO})_5\text{P}$ with appropriate amines similarly gave ArN:P(OPh)_3 : $p\text{-O}_2\text{NC}_6\text{H}_4$, 62%, m. $76-8^\circ$; $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3$, 80%, m. $77-9^\circ$; 3,4-isomer, a liquid, undistillable in vacuo; 5-nitro-2-pyridyl, 60%, m. $58-60^\circ$; $2,4,6\text{-(O}_2\text{N)}_3\text{C}_6\text{H}_2$, 72%, m. $98-100^\circ$. Heating an equimolar mixt. of $(\text{PhO})_3\text{PCl}_2$ and PhSO_2NH_2 at 160° 1.5 hrs., cooling and adding H_2O gave $\text{PhSO}_2\text{N:P(OPh)}_3$, m. $85-6^\circ$, which was washed with aq. NaOH for purification after which it was ~~xxxx~~ recrystd. from EtOH . The same product forms from $(\text{PhO})_5\text{P}$ in a similar reaction, some 80% PhOH being recovered by distn. in vacuo at $140-50^\circ$. Similar reaction with $\text{SO}_2(\text{NH}_2)_2$ gave $\text{SO}_2(\text{N:P(OPh)}_3)_2$, 50-63%, m. $132-4^\circ$. Heating equimolar mixt. of $(\text{PhO})_5\text{P}$ and $(\text{PhO})_2\text{PONH}_2$ 0.5 hr. at $140-50^\circ$ in vacuo (78% PhOH distd.), followed by soln. in hot C_6H_6 , filtration and pptn. with petr. ether, gave 44% $(\text{PhO})_2\text{P(O)N:P(OPh)}_3$, m. $72-4^\circ$. Similarly was prepd. 80% $(\text{PhO})_2\text{P(S)N:P(OPh)}_3$, m. $96-8^\circ$. To 0.01 mole $(\text{PhO})_3\text{P:NPh}$ there was added 20 ml. 50% EtOH ; in 2-3 min. the liquid

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mixt. gave crystalline $(\text{PhO})_2\text{P}(\text{O})\text{NHAr}$ ($\text{Ar}=\text{Ph}$), m. $129-30^\circ$; similarly were obtained: 98% $\text{Ar}=\text{p-O}_2\text{NC}_6\text{H}_4$, m. $146-8^\circ$; 92% $2,4-(\text{O}_2\text{N})_2\text{C}_6\text{H}_3$, m. $144-6^\circ$; 42% $3,4-(\text{O}_2\text{N})_2\text{C}_6\text{H}_3$, m. $143-5^\circ$, and 40% 5-nitro-2-pyridyl, m. $188-90^\circ$. The latter reactions with EtOH were run with heating and brief heating in EtOH contg. a few drops of 10% HCl.

Esters of urethanephosphoric acids.

A. V. Kirsanov and M. S. Marenets (Inst. Org. Chem., Kiev). Zhur. Obshchei Khim. 29, 2256-62 (1959). cf. this j.26, 2642(1956).

An improved prepn. of $\text{MeO}_2\text{CNHPO}(\text{OMe})_2$, a very active systemic insecticides that is nontoxic to animals (K-20-35 or Kiev-20-35) is reported. A mixt. of 1 mole powd. PCl_5 and 1 mole MeO_2CNH_2 was stirred until a homogeneous mass formed (5 min.) and treated with 2 moles MeO_2CNH_2 and 2 moles PCl_5 , this addn. being repeated 5 min. later the flask being warmed to $35-40^\circ$ (bath) or 5° (internally) under vacuum to facilitate the loss of HCl ; after 1 hr. the wt. of the mixt. should not exceed the wt. of 5 moles of $\text{MeO}_2\text{CN}:\text{PCl}_3$ by more than 20 g.; this product may be stored in dry atm. at below 10° but decamps. vigorously above 22° (may be explosive). Similarly were prepd. the analogous Et, iso-Pr, Pr, iso-Bu and Bu esters, which decompose at progressively higher temp. (78° for Bu member). To 1 mole $\text{MeO}_2\text{CN}:\text{PCl}_3$ that had been cooled to -10° there was added 1 mole H_2O maintaining the temp. at under 5° and after 0.5 hr. under vacuo there formed 100% $\text{MeO}_2\text{CNHPOCl}_2$, m. $47-50^\circ$, which reacts rather slowly with moist air and may be stored in dry atm. The other homologs may be prepd. similarly or by the use of 1.05 mole 100% HCO_2H ; thus were prepd. the Et ester, m. $23-5^\circ$; iso-Pr ester, m. $75-7^\circ$; Pr ester, m. 49.50° , iso-Bu and Bu esters, liquids, and C_6H_{11} ester, m. $110-11^\circ$. To 1 mole $\text{MeO}_2\text{CNHPOCl}_2$ in 300 ml. C_6H_6 was added 600 ml. MeOH keeping the temp. under 10° and after 3 hrs. under reduced pressure, finally in a stream of dry air at 30° , a crystn. mass was formed which was taken up in MeOH and treated with 15% NH_3 -MeOH until neutral to Congo red; the soln. was evapd. in vacuo at $30-40^\circ$ yielding 95% crude product which was extd. with 2 l. $(\text{CH}_2\text{Cl})_2$ and evapn. of the ext. gave 80% $\text{MeO}_2\text{CNHPO}(\text{OMe})_2$, m. $63-4^\circ$. The prepn. may be run by addn. of $\text{MeO}_2\text{CN}:\text{PCl}_3$ to large excess of MeOH at 10° . Heating $\text{MeO}_2\text{CN}:\text{PCl}_3$ gave 90% MeCl and 96% OCNPOCl_2 , b₂₀ $45-6^\circ$. Addn. of $\text{RO}_2\text{CNHPOCl}_2$ with 2 moles RONa in C_6H_6 -ROH at below 10° gave after filtration and evapn. $\text{RO}_2\text{CNHPO}(\text{OR}')_2$, uncrystallizable sirups (R and R' = Me to iso-Bu).

No phys. constants are given for these esters and only anal. data are supplied for: (R,R' shown resp.): Me, Me; Me, Et; Et, Me; Et, Et; Et, Pr; Et, iso-Pr; Et, Bu; Et, iso-Bu; Pr, Me; Pr, Et; iso-Pr, Pr; Pr, iso-Pr; Pr, Bu; iso-Pr, Me; iso-Pr, Et; Bu, Me; Bu, Et; Bu, Pr; iso-Bu, Me; iso-Bu, Pr; iso-Bu, iso-Pr; and C_6H_{11} , Me. The proof of structure of these lies in thermal decompn.; thus $EtO_2CNHPO(OMe)_2$ gave EtOH and $OCNPO(OMe)_2$ in 80% yield. The most active insecticide in the group was $iso-PrO_2CNHPO(OMe)_2$.

organophos

Reaction of phosphorus pentachloride with N-chloro derivatives of aromatic sulfonamides.

E. S. Levchenko and A. V. Kirsanov (Inst. Org. Chem., Kiev). Zhur. Obshchei Khim. 29, 1813-14 (1955). cf. this j. 27, 3078(1957).

To 0.03 mole $\text{ArSO}_2\text{NNaCl}$ suspended in CCl_4 there was added 0.03 mole PCl_5 and after 2-3 hrs. the mixt. was filtered and evapd. yielding $\text{ArSO}_2\text{N:PCl}_3$ (Ar shown): Ph, 88%, m. 50-5°; p- MeC_6H_4 , 94%, m. 106-8°; p- $\text{C}_6\text{H}_4\text{Cl}$, 100%, m. 69-71°; m- $\text{C}_6\text{H}_4\text{NO}_2$, 100%, m. 78-80°. Reaction of 0.03 mole $\text{ArSO}_2\text{NCl}_2$ with 0.03 mole PCl_5 in 30 ml. CCl_4 24 hrs. at room temp. gave after eva n. in vacuo: 98% Ph $\text{SO}_2\text{N:PCl}_3$, 94% p-chloro analog, and 100% m-nitro analog, identical with the above. The latter method results in evolution of free Cl_2 which is readily observed during the reaction.

O-Phosphinyl-P,P-diaryloxyisophosphazocaroyls.

G. I. Derkach and A. V. Kirsanov (Inst. Org. Chem., Kiev). Zhur. Obshchei Khim. 29, 1815-18 (1959). cf. this j. 29, 241 (1959) and 29,600(1959). To 0.02 mole PhCCl:NPO(OPh)_2 cooled to -15° there was added 0.2 mole PhP(OEt)_2 (exothermic) and after the initial reaction had subsided, the mixt. was heated 40-50 min. to $80-100^\circ$, yielding 95% EtCl ; after an evacuation to remove residual EtCl , the residue was treated with 2-3 ml. Et_2O and 2 ml. petr. ether, yielding 51% $\text{PhC(P(O)PPh(OEt))NPO(OPh)}_2$, m. $104-5^\circ$ (from CCl_4). Similarly PhP(OMe)_2 gave 100% $\text{PhC(P(O)Ph(OMe))NPO(OPh)}_2$, sirup; this prepn. is best run by addn. of the phosphinite under vacuum of about 10 mm. to facilitate the reaction at $50-60^\circ$. Similarly were prepd.: $\text{PhC(P(O)Ph}_2\text{))NPO(OPh)}_2$, m. $123-5^\circ$; $\text{PhC(P(O)(OEt)}_2\text{))NPO(OPh)}_2$, liquid sirup; $p\text{-ClC}_6\text{H}_4\text{C(P(O)Ph(OEt))NPO(OPh)}_2$, m. unstated, a glassy mass; $p\text{-ClC}_6\text{H}_4\text{C(P(O)Ph(OMe))NPO(OPh)}_2$, a sirup; $p\text{-ClC}_6\text{H}_4\text{C(P(O)Ph}_2\text{))NPO(OPh)}_2$, sirup; $p\text{-ClC}_6\text{H}_4\text{C(P(O)(OEt)}_2\text{))NPO(OPh)}_2$, sirup; $\text{PhC(P(O)Ph}_2\text{))NPO(OC}_{10}\text{H}_7\text{-1)}_2$, glass, m. $48-52^\circ$. Slow addn. of 0.02 mole H_2O with good stirring to 0.02 mole Ph_2PCl in 30 ml. CCl_4 and continued stirring at room temp. 6 hrs., followed by evapn. of CCl_4 in vacuo gave a sirup which crystallized in 12 hrs. to Ph_2PHO , m. $53-6^\circ$ (from Et_2O ; 96%) (cf. Hunt et al. J.Chem.Soc.1957, 2413). This with I_2 in H_2O at pH 6 is converted to $\text{Ph}_2\text{PO}_2\text{H}$, the same being accomplished by treatment with 30% H_2O_2 . The esters shown above are hydrolyzed by aq. EtOH rather slowly to ArCONHPO(OAr)_2 . This requires 4-6 hrs. at room temp. or 1 hr. at reflux. In dil. HCl the hydrolysis proceeds to free ArCO_2H .

*Santhos***Esters of N-arylthiocarbamido-N'-phosphoric acids.**

E. S. Levchenko and I. E. Sheinkman (Inst. Org. Chem., Acad. Sci., Kiev). Zhur. Obshchei Khim. 29, 1249-54 (1959). cf. Levchenko and I. N. Zhmurova, Ukrain. Khim. Zhur. 22, 623 (1956).

In view of insecticidal and tuberculostatic properties found in $(\text{EtO})_2\text{P}(\text{O})\text{NHCSNHPh}$, the following series of esters was prepd. Addn. of equimolar amt. of an amine in Et_2O to $(\text{RO})_2\text{P}(\text{O})\text{NCS}$, followed by several hrs. at room temp. gave the following esters which either pptd. directly or were extd. with N MeOH and the ext. acidified: $(\text{EtO})_2\text{P}(\text{O})\text{NHCSNHR}$ (R shown): o-tolyl, 64.7%, m. $132-3^\circ$; p-tolyl, 53.6%, m. $117-8^\circ$; o- HOC_6H_4 , 83.2%, m. $129-30^\circ$; p- HOC_6H_4 , 55.4%, m. $112-3^\circ$; o- ClC_6H_4 , 47%, m. $126-7^\circ$; m- ClC_6H_4 , 42%, m. $108-10^\circ$; p- ClC_6H_4 , 74.3%, m. $131-2^\circ$; p- FC_6H_4 , 48.6%, m. $133-4^\circ$; p- EtOC_6H_4 , 57.3%, m. $130-1^\circ$; m- HOC_6H_4 , 41.8%, m. $118-20^\circ$; p- $\text{H}_2\text{NSO}_2\text{C}_6\text{H}_4$, 45%, m. $131-2^\circ$; o- HSC_6H_4 , 99%, dec. $108-10^\circ$; 3,4- $(\text{HO})\text{NaO}_2\text{CC}_6\text{H}_3$ (I), 70.3%, dec. $130-1^\circ$; Ph, 25.6%, m. $124-5^\circ$; $(\text{PhO})_2\text{P}(\text{S})\text{NHCSNHC}_6\text{H}_4\text{SH-o}$, 90.4%, dec. $113-5^\circ$; $(\text{PhO})_2\text{P}(\text{S})\text{NHCSNHC}_6\text{H}_4\text{SH-o}$ (II), 77%, dec. $110-11^\circ$. Heating I to $120-5^\circ$ gave H_2S and 90% di-Ph N-2-benzothiazolylphosphoramidate, m. $153-4^\circ$. Similarly was prepd. the di-Et ester, isolated as the picrate, m. $158-61^\circ$. Heating II to 120° gave di-Ph N-2-benzothiazolylphosphorothioamidate, 94.5%, m. $154-5^\circ$. Treatment of $(\text{iso-BuO})_2\text{P}(\text{O})\text{NCS}$ with o- $\text{HSC}_6\text{H}_4\text{NH}_2$ in Et_2O over 2 days yielded the unstable linear product which cyclized directly with loss of H_2S and yielded 73% di-iso-Bu N-2-benzothiazolylphosphoramidate, m. $119-20^\circ$. Similarly $(\text{PhO})_2\text{P}(\text{S})\text{NCS}$ and o- $\text{HOC}_6\text{H}_4\text{NHMe}$ in Et_2O gave 58% di-Ph N-3-methyl-2-benzothiazolidenephosphorothioamidate, m. $147-9^\circ$ (from EtOH). $(\text{EtO})_2\text{P}(\text{O})\text{NCS}$ and 2-aminopyridine in Et_2O gave 90% di-Et N-2-pyridylthiocarbamido-N-phosphate, m. $133-4^\circ$ (from EtOH). $(\text{EtO})_2\text{P}(\text{O})\text{NCS}$ and 3-methyl-2-benzthiazoliminine similarly gave 76.5% di-Et N-3-methyl-2-benzothiazolidenethiocarbamido-N-phosphate, m. $152-3^\circ$. Reaction of $(\text{PhO})_2\text{P}(\text{O})\text{NCS}$ with 2 moles of 2-aminobenzothiazole in Et_2O gave a ppt. of 2-aminobenzothiazole thiocyanate and di-Ph N-2-benzothiazolylphosphoramidate; the former was leached out with H_2O , leaving 70.3% of the latter, m. $153-4^\circ$. The former salt,

m. 136-7°. Similarly 2-aminobenzothiazole and $(\text{EtO})_2\text{P}(\text{O})\text{NCS}$ gave 98% yield of the ~~isomeric~~ above salt, m. 136-7°, only. Di-Et N-2-benzothiazolylphosphoramidate is an undistillable liquid, sol. in bases and acids. All the above products had a weak insecticidal and tuberculostatic activities. The sole substance with appreciable insecticidal activity was $(\text{EtO})_2\text{P}(\text{O})\text{NHCSNHC}_6\text{H}_4\text{Cl-p}$, while $(\text{EtO})_2\text{P}(\text{O})\text{NHCSNEPh}$ had considerable anti-tubercular activity.